The Chemistry of Cyclopropylarene Radical Cations

by

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Cyclopropane derivatives are frequently utilized as “probes” for radical cation intermediates in a number of important chemical and biochemical oxidation. The implicit assumption in such studies is that if a radical cation is produced, it will undergo ring opening. Through a detailed examination of follow-up chemistry of electrochemically and chemically generated cyclopropylarene radical cations, we have shown that the assumption made in the use of these substrates as SET probes is not necessarily valid. While cyclopropylbenzene radical cation undergoes rapid methanol-induced ring opening (e.g., $k = 8.9 \times 10^7 \text{s}^{-1} \text{M}^{-1}$), the radical cations generated from 9-cyclopropylanthracenes do not undergo cyclopropane ring opening at all. The radical cations generated from cyclopropynaphthalenes disproportionate or dimerize before undergoing ring opening. Utilizing cyclic, derivative cyclic, and linear sweep voltammetry, it was discovered that decay of radical cations generated from cyclopropynaphthalenes in CH$_3$CN/CH$_3$OH is second order in radical cation and zero order in methanol. Anodic and Ce(IV) oxidation of all these naphthyl substrates in CH$_3$CN/CH$_3$OH led to cyclopropane ring-opened products. However, the rate constant for methanol-induced ring opening ($\text{Ar-c-C}_3\text{H}_5^+ + \text{CH}_3\text{OH}$ →)
ArCH(•)CH₂CH₂O(H⁺)CH₃ is extremely small (<20 s⁻¹ M⁻¹ for 1-cyclopropynaphthalenes) despite the fact that ring opening is exothermic by nearly 30 kcal/mol. These results are explained on the basis of a product-like transition state for ring opening wherein the positive charge is localized on the cyclopropyl group, and thus unable to benefit from potential stabilization offered by the aromatic ring. Reactions of radical cations generated from 9-cyclopropylanthracenes in CH₃CN/CH₃CN have also been investigated electrochemically. The major products arising from oxidation of these anthryl substrates are attributable to CH₃OH attack at the aromatic ring rather than CH₃OH-induced cyclopropane ring opening. Ce(IV) oxidation of 9-cyclopropyl-10-methylanthracene and 9,10-dimethylanthracene further showed that radical cations generated from these anthryl substrates undergo neither cyclopropane ring opening nor deprotonation but nucleophilic addition. Side-chain oxidation products from Ce(IV) oxidation of methylated anthracenes arose from further reaction of nuclear oxidation products under acidic and higher temperature conditions. An analogous (more product-like) transition state picture can be applied for cyclopropane ring opening and deprotonation of these anthryl radical cations. Because of much higher intrinsic barrier to either nucleophile-induced cyclopropane ring opening or deprotonation of these anthryl radical cations, nucleophilic addition predominates. Stereoelectronic effects may be another additional factor contributing to this intrinsic barrier because the cyclopropyl group in these anthryl systems adopts a perpendicular conformation which may not meet the stereoelectronic requirements for cyclopropyl ring opening at either the radical cation or dication stage.
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# TABLE OF CONTENTS

## Chapter 1. Historical

1.1 Introduction ........................................................................................................ 1

1.1.1 Generation, Detection and Methods for Studying Radical Cations ...... 1

1.1.2 Properties and Reactions of Radical Cations ........................................ 4

1.2 Background ........................................................................................................ 8

1.2.1 Ring Opening Reactions of Cyclopropylarene Radical Cations .......... 8

1.2.2 Deprotonation Reactions of Alkylarene Radical Cations .................. 20

1.3 Dissertation Description ............................................................................... 29

## Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

2.1 Introduction ........................................................................................................ 35

2.2 Results and Discussion .................................................................................... 40

2.2.1 Kinetic Analysis from Voltammetry ...................................................... 40

2.2.2 Product Analysis from Preparative Electrolysis .................................. 69

2.2.3 Reaction Mechanism .............................................................................. 71

2.2.4 Stereoelectronic vs. Thermodynamic Factors ...................................... 77

2.3 Summary .......................................................................................................... 89

## Chapter 3. Cerium (IV) Oxidation of Cyclopropylbenzenes and Cyclopropynaphthalenes

........................................................................................................................... 91
5.2.1 9-Cyclopropylanthracene and 9-Bromo-10-cycloproylantracene ..... 151
5.2.2 9-Cyclopropyl-10-methylanthracene and 9,10-Dimethylantracene ... 157
5.2.3 Nuclear vs. Side-Chain Oxidation ....................................... 163
5.3 Summary .................................................................................... 172

Chapter 6. Conclusion ................................................................. 174

Chapter 7. Experimental ............................................................. 180

7.1 General ..................................................................................... 180

7.1.1 Instrumentation Description ............................................... 180
7.1.2 Electrochemical Experiments .............................................. 181
7.1.3 Materials and Purification ................................................... 183

7.2 Synthesis of Starting Materials ................................................. 184

7.2.1 Cyclopropylanthracenes ..................................................... 184
7.2.2 Cyclopropynaphthalenes ................................................... 186
7.2.3 1-Cyclopropyl-4-methylbenzene ......................................... 191

7.3 Electrolysis of Cyclopropylarenes .......................................... 192

7.3.1 Cyclopropylanthracenes ..................................................... 192
7.3.2 Cyclopropynaphthalenes ................................................... 197

7.4 CAN Oxidation of cyclopropylarenes ...................................... 201

7.4.1 Cyclopropylbenzenes ........................................................ 201
7.4.2 Cyclopropynaphthalenes ................................................... 204
7.4.3 Cyclopropylanthracenes ..................................................... 209
LIST OF SCHEMES

Scheme 1-1. Acidity comparison between toluene and its radical cation .............. 4
Scheme 1-2. Typical reactions of organic radical cations ............................... 5
Scheme 1-3. Anodic oxidation of cyclopropylbenzene and derivatives in CH$_3$OH ... 9
Scheme 1-4. Anodic oxidation mechanism of cyclopropylbenzene in CH$_3$OH ...... 10
Scheme 1-5. Electrochemical oxidation of 1,1,2,2-tetraphenylcyclopropane ........... 12
Scheme 1-6. DCB sensitized photolysis of cyclopropylbenzenes
in CH$_3$CN/CH$_3$OH ................................................................. 13
Scheme 1-7. Two mechanisms for ring opening of cyclopropylbenzene
radical cations ................................................................. 14
Scheme 1-8. Photolysis of cyclopropylbenzenes in the presence of nucleophiles ... 15
Scheme 1-9. Cycloaddition of photogenerated NMP$^-$ to cyclopropylbenzene
radical cation ................................................................. 18
Scheme 1-10. Ce(IV) oxidation of cyclopropylbenzenes in CH$_3$CN and in AcOH 20
Scheme 1-11. Two competing reaction pathways of 9-methylanthracene
radical cation ................................................................. 28
Scheme 1-12. Radical cation rearrangement used as “designer probes” for SET .... 29
Scheme 1-13. Free radical and ketyl anion rearrangement ............................ 30
Scheme 1-14. Free radical bromination of cyclopropylarenes ...................... 31
Scheme 1-15. Lowest energy conformations of cyclopropylarenes ............... 32
Scheme 1-16. Stereoelectronic effects on the chemoselectivity of the free radical
bromination of cyclopropylarenes ......................................... 33

Scheme 1-17. Substrates used in studies on chemistry of cyclopropylarene radical cations .................................................. 34

Scheme 2-1. Rate law expression for decay of radical cation B ................. 38

Scheme 2-2. Anodic oxidation of 1 in CH₃CN/CH₃OH ................................ 69

Scheme 2-3. Anodic oxidation of 2 in CH₃CN/CH₃OH .............................. 70

Scheme 2-4. Anodic oxidation of 3 in CH₃CN/CH₃OH .............................. 71

Scheme 2-5. Anodic oxidation mechanism of 1 in CH₃CN/CH₃OH (dimerization) .. 72

Scheme 2-6. Ring opening mechanism of dimer dication 10 in CH₃CN/CH₃OH ..... 73

Scheme 2-7. Anodic oxidation mechanism of 1 in CH₃CN/CH₃OH (disproportionation) .................................................. 73

Scheme 2-8. Anodic oxidation mechanism of 2 in CH₃CN/CH₃OH .................. 74

Scheme 2-9. Anodic oxidation mechanism of 3 in CH₃CN/CH₃OH .................. 77

Scheme 2-10. Scheme for estimate of rate constant for CH₃OH-induced ring opening of 2⁺. .................................................. 78

Scheme 2-11. Thermodynamic cycle for calculation of DG₀ .......................... 80

Scheme 2-12. Methanol-induced ring opening of cyclopropylarene radical cation ... 85

Scheme 2-13. Ring opening of cyclopropylphenylketel radical anion ............... 88

Scheme 3-1. Synthesis of 1-cyclopropyl-4-methylbenzene (2) ....................... 93

Scheme 3-2. Synthesis of 1-cyclopropynaphthalene (3) and

1-bromo-4-cyclopropynaphthalene (4) ........................................ 94

Scheme 3-3. Ce(IV) oxidation of 1-cyclopropylbenzene (1) in CH₃CN ............. 95

Scheme 3-4. Ce(IV) oxidation of 1-cyclopropyl-4-methylbenzene (2) in CH₃CN ... 95
Scheme 3-5. Ce(IV) oxidation of toluene in CH₃CN .......................... 96
Scheme 3-6. Ce(IV) oxidation of 1-cyclopropynaphthalene (3) in CH₃CN/CH₃OH 97
Scheme 3-7. Ce(IV) oxidation of 1-bromo-4-cyclopropynaphthalene (4) in CH₃CN/CH₃OH ................................................................. 98
Scheme 3-8. Ce(IV) oxidation of 2-cyclopropynaphthalene (5) in CH₃CN/CH₃OH 98
Scheme 3-9. Ce(IV) oxidation of 1-methylnaphthalene in CH₃CN/CH₃OH .......... 99
Scheme 3-10. Ce(IV) oxidation mechanism of 1-methyl-4-cyclopropylbenzene (2) 100
Scheme 3-11. Ce(IV) oxidation mechanism of 1-cyclopropynaphthalene (3) .... 101
Scheme 3-12. The alternative mechanisms for oxidation of
1-cyclopropynaphthalene (3) ...................................................... 102
Scheme 4-1. Anodic oxidation of 2 in CH₃CN/CH₃OH .............................. 120
Scheme 4-2. Conversion of product 3 to product 4, 5, or 6 in acidic condition .... 122
Scheme 4-3. Anodic oxidation mechanism of 1 (from 1 to 7) ...................... 125
Scheme 4-4. Anodic oxidation mechanism of 1 (from 7 to 3) ...................... 126
Scheme 4-5. Anodic oxidation mechanism of 2 ........................................ 128
Scheme 4-6. Ring opening mechanism of 3 under acidic condition ............... 129
Scheme 4-7. Stereoelectronic effects on reactivity of cyclopropylarene
radical cations ................................................................. 134
Scheme 4-8. Stability of benzylic-type radical and cyclohexadienyl-type radical .... 135
Scheme 5-1. Anodic oxidation of anthracene and substituted anthracenes .......... 143
Scheme 5-2. Lead tetraacetate oxidation of DMA and proposed mechanism ....... 144
Scheme 3-3. Fe(III) oxidation of 9,10-dialkylanthracenes in CH₃CN/H₂O .......... 145
Scheme 5-4. Iodine oxidation of 9-alkyl-, and 9-alkyl-10-methyl-anthracenes ..... 146
Scheme 5-5. Iodine oxidation of aceanthracene and 9-methylaceanthracene ....... 146
Scheme 5-6. Ce(IV) oxidation of alkylanthracenes in CH$_3$CN/H$_2$O .................. 147
Scheme 5-7. Cu$^{2+}$-S$_2$O$_8^{2-}$ oxidation of 9-methylanthracene ...................... 148
Scheme 5-8. Cu$^{2+}$-S$_2$O$_8^{2-}$ oxidation of DMA and 9-phenylethylanthracene ....... 149
Scheme 5-9. Oxidation of anthracenes and substituted anthracenes ................. 150
Scheme 5-10. Ce(IV) oxidation of 1 in CH$_3$CN/H$_2$O .................................. 152
Scheme 5-11. Ce(IV) oxidation of 2 in CH$_3$CN/CH$_3$OH .............................. 154
Scheme 5-12. Proposed mechanism of Ce(IV) oxidation of 1 and 2 ................... 156
Scheme 5-13. Ce(IV) oxidation of 3 in CH$_3$CN/CH$_3$OH .............................. 157
Scheme 5-14. Ce(IV) oxidation of 4 in CH$_3$CN/CH$_3$OH .............................. 159
Scheme 5-15. Ce(IV) oxidation of 4 in CH$_3$CN ........................................... 160
Scheme 5-16. Control experiment to test whether 10 can be converted into

"deprotonation" product 9 under conditions of Ce(IV) oxidation ... 162
Scheme 5-17. Oxidation mechanism of 4 in CH$_3$CN/CH$_3$OH ....................... 163
Scheme 5-18. Nucleophilic addition vs. deprotonation of toluene radical cation ... 166
Scheme 5-19. Mechanism for the conversion (10 → 9) under acidic condition .... 169
Scheme 5-20. Mechanism of solvolysis of 9,10-diethyl-9,10-dihydroxyanthracene

in H$^+$/H$_2$O ................................................................. 170
Scheme 5-21. Possible decay pathways of 9-cyclopropyl-10-methylanthracene

radical cation .............................................................. 171
Scheme 6-1. Decay pathways of 9-cyclopropyl-10-methylanthracene radical cation

in CH$_3$CN/CH$_3$OH ...................................................... 178
LIST OF FIGURES

Figure 2-1. Cyclic voltammogram of 1 in CH$_3$CN  ........................................ 40
Figures 2-2→2-13. LSV analysis of 1  ................................................................. 42→47
Figure 2-14. Cyclic voltammogram of 2 in CH$_3$CN  ........................................ 48
Figures 2-15→2-31. LSV analysis of 2  ................................................................. 50→58
Figure 2-32. Cyclic voltammogram of 2 in CH$_2$Cl$_2$  ....................................... 59
Figures 2-33→2-35. DCV analysis of 2  ................................................................. 60→61
Figure 2-36. Dimensionless working curve for Ec$_{dim}$ mechanism .................. 62
Figure 2-37. Cyclic voltammogram of 3  .............................................................. 63
Figures 2-38→2-46. LSV analysis of 3, $\partial E/P/\partial \log[3]$  .................................. 65→68
Figure 2-47. Variation of $k_{dim}$ for 2$^{*\bullet}$ with [CH$_3$CN] in CH$_2$Cl$_2$ solvent .. 76
Figure 2-48. Comparison of IP’s obtained via AM1 vs. those via experiments ...... 81
Figure 2-49. E$^\circ$ as a function of AM1-calculated IP’s  ...................................... 82
Figure 2-50. The proposed effect of aryl rings on the stabilities of reactants, transition
states and products for CH$_3$OH-assisted cyclopropyl ring opening ..... 87
Figure 4-1. Cyclic Voltammogram of 9-cyclopropylnaphthacene (1) in CH$_3$CN ..... 106
Figures 4-2→4-4. LSV analysis of 1  ................................................................. 107→108
Figure 4-5. Cyclic Voltammogram of 2 in CH$_3$CN (whole view) ...................... 110
Figure 4-6. Cyclic Voltammogram of 2 in CH$_3$CN (partial view) ...................... 110
Figures 4-7→4-8. DCV analysis of 2  ................................................................. 111
Figures 4-9→4-11. LSV analysis of 2 ........................................... 113→114

Figures 4-12→4-15. Variation of the cathodic to anodic current ratio (-I_{pc}/I_{pa}) with
sweeprate for the oxidation of 2 .............................. 115→117

Figure 4-16. I_{p}/C_{o} vs. v^{1/2} plot for 2 at various concentrations of methanol ....... 119

Figure 4-17. I_{p}/C_{o} vs. v^{1/2} plot for 1 in the presence of methanol ....................... 119

Figure 4-18. AM1-predicted geometry for the “bisected” and perpendicular
conformations of 1* .............................................................. 131

Figure 4-19. The proposed effect of aryl rings on the stabilities of reactants, transition
states and products for CH$_3$OH-assisted cyclopropyl ring opening  ... 137

Figure 5-1. $^1$HNMR of 4 (a), reaction mixtures before workup (b) and
after workup (c) ................................................................. 161

Figure 5-2. Proposed effect of different aryl groups on the stabilities of reactants,
transition states, and products for deprotonation of ArCH$_3$* .......... 165

Figure 5-3. Proposed reaction energy diagram of toluene radical cation ............... 167

Figure 5-4. Proposed reaction energy diagram for 9-methylanthracene
radical cation ................................................................. 168

Figure 6-1. The proposed effects of aryl rings on the stabilities of reactants, transition
states and products for methanol-induced cyclopropane ring opening 176
LIST OF TABLES

Table 1-1. Rate constants for the reaction of methanol with various 1,1-diphenyl-2-alkylcyclopropane radical cations in CH$_2$Cl$_2$ at 22 °C ….. 17

Table 2-1. Theoretical LSV and CV (or DCV) responses for rate law of decay of radical cation generated (reversibly) by heterogeneous electron transfer (25 °C) 39

Table 2-2. Observed LSV response for the electrochemical oxidation of 1 in CH$_3$CN ………………………………………………………… 41

Table 2-3. Observed LSV response for the electrochemical oxidation of 2 in several solvent/electrolyte combinations ……………………………….. 49

Table 2-4. Observed DCV response for the electrochemical oxidation of 2 in CH$_2$Cl$_2$ and in the presence of CH$_3$CN or CH$_3$OH …………………….. 59

Table 2-5. Rate constants for dimerization of 2$^+$ (CH$_2$Cl$_2$ solvent mixed with varying amounts of CH$_3$OH or CH$_3$CN) ……………………………….. 63

Table 2-6. Observed LSV response for the electrochemical oxidation of 3 in CH$_3$CN ………………………………………………………………….. 64

Table 2-7. Oxidation potentials and AM1-calculated ionization potentials for several aromatic hydrocarbons …………………………………………. 82

Table 2-8. $\Delta G^0$ for the methanol-induced ring opening of cyclopropylarene radical cations in CH$_3$CN ………………………………………………. 83

Table 4-1. LSV analysis of the electrochemical oxidation of 1 …………………….. 109

Table 4-2. DCV analysis of the electrochemical oxidation of 2 …………………….. 112
Table 4-3. LSV analysis of the electrochemical oxidation of 2 ………………… 114
Table 4-4. Yields of products produced in the controlled-current oxidation of 2 121
Table 4-5. Yields of products produced in the controlled-current oxidation of 1 123
Table 4-6. AM1-calculated $\Delta H^0$ for conformational interconversion (perpendicular $\rightarrow$ bisected) for the 9-cyclopropylanthracene and cyclopropylbenzene system 130
Table 4-7. $\Delta G^0$ for the methanol-induced ring opening of cyclopropylarene radical cations in CH$_3$CN …………………………………………………. 136
Table 5-1. Product yields of Ce(IV) oxidation of 1 in CH$_3$CN/CH$_3$OH ………… 152
Table 5-2. Product distribution of Ce(IV) oxidation of 1 in different mole ratio of Ce(IV) to 1 …………………………………………………………….. 153
Table 5-3. Product yields of Ce(IV) oxidation of 2 in CH$_3$CN/CH$_3$OH ………… 154
Table 5-4. Product yields of Ce(IV) oxidation of 3 in two reaction conditions ….. 158
Table 5-5. Product yields of Ce(IV) oxidation of 4 in different conditions ………. 159
CHAPTER 1. HISTORICAL

1.1 INTRODUCTION

Organic radical cations, their structures and their reactions have been attracting ever increasing attention for the last two decades.\(^1\)\(^2\) Radical cations are important intermediates in a variety of chemical and biological processes, encompassing photosynthesis\(^3\) and interstellar chemistry\(^4\) and ranging from conducting polymers\(^5\) to synthetically useful reactions, such as electron transfer induced anti-Markovnikov additions,\(^6\) radical cation Diels-Alder reactions,\(^7\) or nucleophilic substitution reactions.\(^8\)

“The Formation, Properties and Reactions of Radical Cations in Solution” was extensively reviewed by Bard et al. in 1976.\(^9\) Since then, there have been a number of other good reviews such as “Electron Transfer Reactions in Organic Chemistry” by Eberson (1982),\(^10\) “The Kinetics and Mechanism of Reactions of Organic Cation Radicals in Solution” by Hammerich and Parker (1984),\(^11\) and “The Structure and Reactivity of Organic Radical Cations” by Roth (1992).\(^12\) Other important reviews dealing with cyclopropane chemistry are “Photochemistry of Cyclopropanes” by Hixson (1979)\(^13\) and “Cyclopropane Radical Cations” by Boche and Walborsky (1990).\(^14\)

1.1.1 Generation, Detection and Methods for Studying Radical Cations

**Generation.** A radical cation is generated by the removal of one electron from a neutral molecule. The resulting species is at the same time a cation (the positive charge
caused by the loss of an electron) and a radical (the remaining unpaired electron). One-electron oxidation can be achieved by a variety of methods such as chemical oxidation, photochemical oxidation, electrochemical oxidation, and other methods like pulse radiolysis and electron impact ionization.

**Chemical Oxidation.** A variety of chemical oxidizing reagents has been applied for the generation of radical cations. The principal types of reagents include: Bronsted and Lewis acids; the halogens; certain peroxide anions or radical anions; numerous metal ions or oxides; nitrosonium and dioxygenyl ions; stable organic (aminium) radical cations; some semiconductor surfaces; and certain zeolites.

**Photochemical Oxidation.** A mild and versatile method for the generation of radical cation-radical anion pairs in solution is based on photoinduced electron transfer (PIET). This method utilizes the fact that the oxidative power of an acceptor or the reductive power of a donor is substantially enhanced by photoexcitation. Thus, for donor and acceptor pairs with negligible or weak interactions in the ground state, electronic excitation of either reactant may lead to the generation of radical ion pairs via electron transfer. The resulting pairs have limited lifetimes since they readily undergo intersystem crossing and recombination. For the study of radical cations it is advantageous to excite the acceptor. Singlet excited state electron acceptors are likewise used as organic photooxidants. The most frequently used singlet state electron acceptors are aromatic hydrocarbons bearing one or more cyano groups.

**Electrochemical Oxidation.** Anodic oxidation is one of most important methods to generate radical cations. An electrode is fundamentally an electron transfer agent so that, given the proper solvent system, anodic oxidation allows formation of the radical
cation without formation of a reduced species in the immediate vicinity of the radical
cation. Moreover, because the potential of the electrode can be adjusted precisely, its
oxidizing power can be controlled and further oxidation of the radical cation can be
avoided. A variety of electrochemical techniques has been developed for the generation
and study of organic radical cations.\(^{16}\)

**Detection.** The methods for detection of radical cations are mostly physical
methods such as mass spectrometry (MS), ultraviolet photoelectron spectroscopy (UV-
PES), optical spectroscopy, electron spin resonance (ESR), fluorescence detected
magnetic resonance (FDMR), and nuclear magnetic resonance (NMR) methods (e.g.
chemically induced dynamic nuclear polarization, or CIDNP). Among the techniques
available to study free radicals or radical ions in solution, ESR stands out as a technique
with sufficient resolution to provide detailed information about the identity and structure
of the intermediate in question. CIDNP is the technique most recently introduced to study
radical cations. It is based on transient enhanced NMR signals, in absorption or emission,
shown by some diamagnetic products of radical reactions. The signal can be related to \(^1\)H
hyperfine couplings which reveal structural features of the intermediates. The results from
CIDNP can be expected to reflect the equilibrium structure of the intermediates. This
method has been successfully applied to the investigation of cyclopropane radical
cations.\(^{12}\)

**Methods for Studying Radical Cations.** The decay kinetics and mechanism of
radical cations can be studied by laser flash photolysis (LFP), spectroelectrochemistry (e.g.
UV-visible spectroelectrochemistry),\(^{17}\) direct and indirect electrochemistry\(^{18}\) as well as
conventional stop flow method. Electrochemical methods, such as cyclic voltammetry
Chapter 1. Historical

(CV), derivative cyclic voltammetry (DCV), linear sweep voltammetry (LSV),
chronoamperometry and homogenous redox catalysis, have been employed extensively in
studies of follow-up reactions of radical cations. Besides, both the general nature and the
detailed structure of an intermediate are frequently inferred from the reaction conditions
and from the type and structure of the reaction products. Also, molecular orbital
calculations at different levels of sophistication have become an integral part in the
characterization of organic radical cations in general and those of strained molecules like
cyclopropanes in particular.12,14

1.1.2 Properties and Reactions of Radical Cations

Radical cations, like other paramagnetic species such as free radicals or radical
anions, are much more reactive than the corresponding neutral species. A simple change
in oxidation state of a molecule can drastically affect its reactivity. For example, toluene is
an extremely weak acid with a pKa of 41. If toluene is oxidized to its radical cation, its
pKa plummets to –1319 (Scheme 1-1).

![Scheme 1-1. Acidity comparison between toluene and its radical cation](image)

\[
\text{CH}_3\text{CH}_2\overset{+}{\text{H}}^\text{+} \quad \text{pK}_a = 41
\]

\[
\text{CH}_3\text{CH}_2\overset{+}{\text{H}}^\text{+} \quad \text{pK}_a = -13
\]

Scheme 1-1. Acidity comparison between toluene and its radical cation
Organic radical cations undergo a rich variety of reactions, including both unimolecular processes and bimolecular reactions. Among the unimolecular reactions are geometric isomerization, rearrangement, cycloreversion, as well as fragmentation and other bond cleavage reactions. In bimolecular reactions, radical cations can react with neutral reagents, ionic substrates (especially nucleophiles), free radicals and radical ions of like and opposite charge. These reactions include a) ion-molecule reactions, such as cycloadditions, hole transfer, or complex formation; b) nucleophile capture; c) spin labeling; and d) dimerization or disproportionation, and reverse electron transfer, proton transfer, atom or group transfer reactions, or coupling. Some typical reactions of organic radical cations which are frequently met in our studies are shown in Scheme 1-2.

Scheme 1-2. Typical reactions of organic radical cations
Deprotonation. Deprotonation of radical cations in the gas phase is a high energy process due to the formation of a “naked” proton. In solution, however, the large solvation energy of the proton may provide the driving force for radical cation deprotonation, and this reaction is expected to play an important role in the chemistry of a large range of radical cations. The deprotonation of alkylbenzene radical cations has been studied in detail in nonaqueous solvents under aprotic and acidic conditions.

Rearrangement. Unimolecular rearrangements of radical cations, especially of those generated from hydrocarbons containing strained-ring moieties (e.g., cyclopropyl group), have been attracting ever increasing attention over the last two decades. Radical cations generated from strained-ring compounds may undergo rearrangement because of ring strain. Consequently, the unusually low oxidation potential of strained rings were noted.

Disproportionation. In disproportionation, two molecules of radical cation undergo single electron transfer to produce a neutral (parent) molecule and a dication. The reaction is usually detected kinetically, spectroscopically or by electrochemical techniques. Many reactions of radical cations with nucleophiles have the stoichiometry of Eq. 1-1:

\[
2 \text{M}^+ + \text{Nu}^- \rightarrow \text{M} + \text{M-Nu}^+ \quad (1-1)
\]

Without the aid of kinetics it is not possible to say what the mechanism is, and two important possibilities exist, namely, direct reaction with the radical cation (Eq. 1-2 and Eq. 1-3):

\[
\text{M}^+ + \text{Nu}^- \rightarrow \text{M-Nu}^- \quad (1-2)
\]
Chapter 1. Historical

\[ \text{M-Nu}^- + \text{M}^{+} \rightarrow \text{M-Nu}^+ + \text{M} \]  \hfill (1-3)

or reaction with a dication formed via disproportionation (Eq. 1-4 and Eq. 1-5):

\[ 2 \text{M}^+ \rightarrow \text{M} + \text{M}^{2+} \]  \hfill (1-4)

\[ \text{M}^{2+} + \text{Nu}^- \rightarrow \text{M-Nu}^+ \]  \hfill (1-5)

**Dimerization and Complex Formation.** Two molecules of radical cation may
dimerize to form a dimer dication (Eq. 1-6), while a radical cation associates with a parent
molecule to form a complex, dimer radical cation (Eq. 1-7):

\[ 2 \text{M}^+ \rightarrow \text{M-M}^{2+} \]  \hfill (1-6)

\[ \text{M}^+ + \text{M} \rightarrow \text{M-M}^+ \]  \hfill (1-7)

The paramagnetic dimer radical cation is usually characterized by an ESR spectrum with
twice as many lines and half the splitting constant of \text{M}^+, while dimer dication results in
spin pairing and the disappearance of the ESR signal.

**Nucleophilic Reactions.** Radical cations react with a variety of nucleophiles.

There are many reactions named on the basis of the nucleophile involved, such as
hydroxylation, methoxylation, acetoxylation, acetamidation, pyridination, cyanation,
halogenation, etc.. Reactions of these types were classified according to the nature of the
reaction: substitution, addition and electron transfer reaction. By virtue of the fact that
the initial reaction between a radical cation and a nucleophile produces an unstable radical
intermediate, the reactions are inevitably complex. Further electron-transfer reactions
accompanied by a proton transfer or reaction with a nucleophile are necessary in order to
reach a stable product. These multi-step reactions can give rise to complicated rate laws
and the observed mechanism can be highly dependent upon the reaction conditions,
especially on the magnitudes of the concentrations of the reactants. While some
nucleophilic reactions occur at the stage of radical cations (Eq. 1-2), others may occur at
the stage of dication (Eq. 1-5). The detailed mechanisms were discussed by Parker.\textsuperscript{11}
Eberson has provided a theoretical explanation for a number of nucleophilic reactions,
based on the Dewar-Zimmerman rules.\textsuperscript{20}

1.2. BACKGROUND

1.2.1 Ring Opening Reactions of Cyclopropylarene Radical Cations

Among reactions of cyclopropylarene radical cations, cyclopropane ring opening
reactions have been the subject of numerous investigations. The methods for studying
these reactions ranged from anodic oxidation, photoinduced electron transfer to metal-
mediated oxidation. The most frequently employed substrates are cyclopropylbenzene and
its derivatives.

**Electrochemical Oxidation.** Extensive studies have been focused on oxidative
cleavage of cyclopropane rings by electrochemical methods in the past and recent years
because of the unique reactivity of the strained $\sigma$-bonds, easy availability of cyclopropane
compounds and the usefulness of the resulting products in organic synthesis. Anodic
oxidation of cyclopropylbenzene and derivatives in methanol was studied by Shono, et
al.\textsuperscript{21} in 1970. The cyclopropane ring-opened products (1,3-dimethoxy ether) were
obtained from the bulk electrolysis (Scheme 1-3).
Controlled potential oxidation and product analysis suggested that the reaction was initiated by the oxidation of the aromatic nucleus to a radical cation. Half-wave polarographic oxidation potentials of cyclopropylbenzenes were measured in CH$_3$CN and plotted against Hammett’s $\sigma^+$. The results indicated that the electron was transferred to the anode not from the cyclopropane ring but from the phenyl ring, and that opening of the cyclopropane ring was through the conjugate interaction of the cyclopropyl group and adjacent carbonium ion in the intermediate. Thus, the mechanism of oxidation was believed to involve initial one-electron oxidation yielding a radical cation, which subsequently underwent cyclopropane ring opening, as shown in Scheme 1-4.
The anodic oxidation of polyalkyl-substituted cyclopropanes and spiro[2, n]alkanes was carried out in methanol by Shono et al. in 1975. Monomethoxyolefin and dimethoxy compounds resulted from the selective cleavage at the most substituted carbon-carbon bond. In the same year, anodic oxidation of several other cyclopropane derivatives was studied by Klehr et al. and by Brettle et al. Electroylsis of cyclopropylbenzene in methanolic sodium methoxide gave 1,3-dimethoxy-1-phenylpropane, which was also formed together with 3-methoxy-3-phenylpropan-1-ol and 3-methoxy-1-phenylpropan-1-ol in methanolic sodium methyl carbonate. Electrolysis of 2-(2-methyl-1-propenyl)-1,1-dimethylcyclopropane in either system gave 4,6-dimethoxy-2,6-dimethylhept-2-ene and (E)-2,6-dimethoxy-2,6-dimethylhept-3-ene.

In 1985, Uchida, et al. found that anodic oxidation in acetic acid of polycyclic cyclopropanes, namely tricyclene, cyclofenchene, and longicyclene, followed by hydrolysis
brought about stereo- and regioselective formation of the corresponding homoallylic 
alcohols as the main product in good yields (76~85%). Later in 1990, Uchida, et al.\textsuperscript{27} 
reported a facile and efficient synthesis of exo-5,5-dimethyl-6-
methylenebicyclo[2,2,1]heptan-2-ol, named “nojigiku alcohol”, based on the same 
cyclopropane ring opening reaction.

The electrochemical oxidation of 1,1,2,2-tetraphenylcyclopropane was reported in 
detail by Wayner and Arnold.\textsuperscript{28} The products obtained from controlled potential 
electrolysis were 1,3,3-triphenylindene, tetraphenyllallene and 3-methoxy-1,1,3,3-
tetraphenylpropene, depended on the medium systems employed. Studied by cyclic 
voltammetry and other photochemical methods, 1,1,2,2-tetraphenylcyclopropane was 
observed to oxidize irreversibly at 1.36V (in CH\textsubscript{3}CN vs. SCE) via a two-electron process 
leading to 1,1,3,3-tetraphenylpropenyl cation,\textsuperscript{29} which subsequently cyclizes to form 1,3,3-
triphenylindene or deprotonates to give tetraphenyllallene, depending on the basicity of the 
medium, or is captured by methanol to produce 3-methoxy-1,1,3,3-tetraphenylpropene 
(Scheme 1-5). The effects of multiple substitution by methoxy and cyano in the 4-
position(s) of 1,1,2,2-tetraphenylcyclopropane on the oxidation potential have also been 
measured. The results indicated that the oxidation process for the cyclopropanes is 
irreversible and the substituent effect on the potential is essentially additive and correlates 
reasonably well with $\Sigma\sigma^+$. A slow electron transfer process, with a transition state 
resembling the ring-opened radical cation, compromises with this observation (Scheme 1-
5).\textsuperscript{30}
Chapter 1. Historical

**Scheme 1-5. Electrochemical oxidation of 1,1,2,2-tetraphenylicyclopropane**

**Photochemical Oxidation.** For the past decade, much attention has been focused on the reactivity of radical cations generated via photoinduced electron transfer from cyclopropylarenes. The radical cations thus generated are subject to a nucleophilic attack if an appropriate nucleophile is present in the system. Photocleavage of cyclopropane ring in cyclopropylbenzene and derivatives is a subject of increasing interest mainly from mechanistic viewpoints. Rao and Hixson,\(^{31}\) in 1979, reported photolysis of several cyclopropylbenzenes in \(\text{CH}_3\text{OH/CH}_3\text{CN}\) using 1,4-dicyanobenzene (DCB) as a sensitizer. In most cases, a novel “anti-Markownikoff” addition of methanol to the cyclopropane ring resulted (Scheme 1-6).
The reactions observed were best rationalized as proceeding via initial electron transfer from the cyclopropanes to the excited DCB to give the cyclopropylbenzene radical cations. Two mechanisms for cyclopropane ring opening of the intermediate radical cations were proposed: unimolecular rearrangement of the cyclopropylarene radical cation to the ring-opened distonic radical cation ("$S_N1$") and/or methanol induced ("$S_N2$", bimolecular) ring opening (Scheme 1-7).
Although the fact that attack occurs at the most substituted carbon of cyclopropylbenzene radical cation supports “$S_N1$” pathway, the finding that only a very small amount of $trans-cis$ isomerization occurs when $trans$-1-methyl-2-phenylcyclopropane is reacted in the absence of methanol is not readily accommodated by this mechanism. Most likely the radical cation of $trans$-1-methyl-2-phenylcyclopropane undergoing attack by methanol has a significantly weakened yet not broken $C_1$-$C_2$ bond.

Mizuno, al et.\textsuperscript{32} independently reported their results on the polar addition of various nucleophiles to cyclopropylarenes through a photoinduced electron transfer and on the reactivity feature of radical cations produced as intermediates. Mizuno, al et.\textsuperscript{33} also in 1981 reported the photoinduced nucleophilic attack of methanol on cyclopropylbenzene in the presence of copper (II) ions, which proceed via one-electron transfer from excited substrate to Cu(II) ions. The 1,3-dimethoxy-1-phenylpropane was isolated as major
product in this reaction (70%). Later in 1983, Mizuno, al et.\textsuperscript{34} reported in detail the 9,10-dicyanoanthracene (DCA)-sensitized two-electron oxidation of cyclopropylbenzene and aromatic olefins in the presence of Cu(II) ions, in which 1,3-dimethoxy-1-phenylpropane was formed in a yield of 84%.

Based upon the work of Rao and Hixson, several cyclopropylarenes were chosen by Dinnocenzo, et al.\textsuperscript{35} as substrates for determining the stereochemistry of nucleophilic one-electron \(\sigma\)-bond cleavage. The 1-cyanonaphthalene (1-CN) photosensitized oxidation of these cyclopropylarenes in the presence of nucleophiles (e.g., CH\(_3\)OH, H\(_2\)O, KCN) yielded exclusively ring opened products. The reactions were characterized as occurring with essentially complete inversion of configuration at carbon undergoing nucleophilic substitution, based on stereochemical analysis of the products (Scheme 1-8).

![Scheme 1-8. Photolysis of cyclopropylbenzenes in the presence of nucleophiles](image-url)
This observation was consistent with a ring-closed radical cation intermediate proposed by Rao and Hixson.\textsuperscript{31} There were other reports dealing with ring-closed radical cations and nucleophilic substitution with inversion of configuration.\textsuperscript{36} The explanation as to why these nucleophilic cleavage reactions proceed with inversion of configuration was provided by the valence-bond curve crossing model.\textsuperscript{37} The model predicts that the stereochemical course of nucleophilic displacements on $\sigma$ one electron bonds will be governed by the $\sigma^*$ (LUMO) orbital of the one-electron bond and will therefore proceed with conversion of the configuration at the site of attack.

The rate constants for the alcohol cleavage of the one-electron $\sigma$-bond in the cyclopropylbenzene radical cation was measured in CH$_3$CN, CH$_2$Cl$_2$ and dichloroethane by laser flash photolysis.\textsuperscript{38} The detailed mechanism for three-electron $S_N2$ reactions of cyclopropylarene radical cations was reported.\textsuperscript{38}

In 1993, Dinnocenzo and coworkers\textsuperscript{39} reported several examples of three-electron $S_N2$ reactions that exhibit greatly diminished steric effects and occur with preferential substitution at the more hindered carbon atom, even when it is tertiary or neopentyl. The 1-cyanonaphthalene-sensitized photooxidations of 1,1-diphenyl-2-methylcyclopropane, 1,1-diphenyl-2,2-dimethylcyclopropane and 1,1-diphenyl-2-tert-butylcyclopropane in degassed methanol yielded exclusively corresponding cyclopropane ring-opened products (98\%, 93\% and 60\%, respectively) with substitution at more hindered carbon. The steric effects were evaluated by measuring rate constants for the reactions of methanol with various 1,1-diphenyl-2-alkylcyclopropane radical cations with laser flash photolysis (Table 1-1). The data reveal steric effects in the three-electron $S_N2$ reactions much smaller than those found...
in most four-electron $S_N2$ reactions. This can be explained by Hammond’s postulate.\textsuperscript{40} On the basis of the large rate constants for these reactions, an early transition state is expected. The alkyl substituents stabilize positive charge at the carbon atom undergoing substitution, thereby reversing the normal regiochemistry of substitution. The electronic effects apparently overwhelm the smaller steric effects in three-electron $S_N2$ transition states.

Table 1-1 Rate constants for the reaction of methanol with various 1,1-diphenyl-2-alkylcyclopropane radical cations in CH$_2$Cl$_2$ at 22 °C

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Substituents at } C_2 & k (M^{-1}s^{-1}) & k_{rel} \\
\hline
R_1 & R_2 & k \times 10^n & \\
\hline
\text{Me} & \text{H} & 1.5(1) \times 10^8 & 31 \\
\text{Et} & \text{H} & 8.3(4) \times 10^7 & 17 \\
\text{Pr}^i & \text{H} & 3.0(1) \times 10^7 & 6.3 \\
\text{Bu}^i & \text{H} & 4.8(2) \times 10^6 & 1 \\
\text{H} & \text{H} & 1.7(2) \times 10^7 & 1 \\
\text{Me} & \text{H} & 1.5(1) \times 10^8 & 8.8 \\
\text{Me} & \text{Me} & 3.2(1) \times 10^8 & 19 \\
\hline
\end{array}
\]
The detailed studies of steric and electronic effects on the three-electron \( S_N2 \) substitution of cyclopropylarene radical cations were reported recently by Dinuccenzo, et al. using a combination of methods including product analysis, time-resolved laser flash photolysis, kinetic isotope effects and quantum chemical calculations.\(^{41}\)

Mazzochi, al et.\(^{42}\) first reported the cycloaddition of photochemically generated N-methylphthalimide (NMP) and N-methylnaphthalimide (NMN) radical anions to cyclopropylbenzene radical cations to give the corresponding spiroethers. The reaction of NMP radical anion and cyclopropylbenzene radical cation was illustrated in Scheme 1-9. Other research workers\(^ {43}\) also studied electron transfer photoreactions of quinone with cyclopropylbenzenes and similar cycloaddition products were obtained.

\[
\begin{array}{c}
\text{NMP} \\
\text{N} \text{O} \\
\text{N} \text{O} \\
\text{O} \\
\text{O}
\end{array}
\]
\[
\begin{array}{c}
\text{hv} \\
\text{CH}_3\text{CN} \\
\text{NMP} \\
\text{N} \text{O} \\
\text{N} \text{O} \\
\text{O} \\
\text{O}
\end{array}
\]
\[
\begin{array}{c}
\text{hv} \\
\text{CH}_3\text{CN} \\
\text{NMP} \\
\text{N} \text{O} \\
\text{N} \text{O} \\
\text{O} \\
\text{O}
\end{array}
\]
\[
\begin{array}{c}
\text{CH}_3\text{CN} / \text{CH}_2\text{OH} \\
\text{NMP} \\
\text{N} \text{O} \\
\text{N} \text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

Scheme 1-9. Cycloaddition of photogenerated NMP\(^{-} \) to cyclopropylbenzene radical cation
Besides the photoaddition of nucleophiles to cyclopropylarene radical cations, the photosensitized cis \(\rightarrow\) trans isomerization\(^{44}\) and photo-oxygenation\(^{45}\) of 1,2-diphenylcyclopropane (and other disubstituted cyclopropanes) were explained to involve cyclopropane radical cations via photoinduced electron transfer.

**Metal-mediated Oxidation.** Cyclopropane ring cleavage by electrophiles to yield adducts has been known since the 19\(^{th}\) century. Ouellette, al et.\(^{46}\) reported cleavage of cyclopropylbenzene by lead tetraacetate, thallium triacetate and mercuric acetate, and S\(_{E2}\) mechanism for the ring opening was proposed based on kinetic studies. Although electrophilic attack on the cyclopropane ring is well established, very few examples that certain cyclopropanes are readily susceptible to reaction with one-electron oxidizing reagents have been reported. Young\(^{47}\) first reported ceric(IV) ammonium nitrate (CAN) cleavage of of cyclopropylbenzenes and ring opened 1,3-disubstituted products were obtained (Scheme 1-10). Specifically, he found that the Ce(IV) oxidation of 1,1-dimethyl-2-phenylcyclopropane results in exclusively cleavage between the phenyl- and gem-dimethyl-substituted carbons. However, the mechanism of Ce(IV) oxidation of cyclopropylbenzenes remained vague although Young pointed that the reaction pathway of Ce(IV) oxidation of cyclopropanes must be quite different from lead, thallium, and mercury acetate oxidations because Ce(IV) is not amenable to metal-carbon bond formation.
1.2.2 Deprotonation of Alkylarene Radical Cations

The side-chain oxidation of alkyl aromatic compounds is one of the most important organic reactions and accordingly, it has been the subject of intense investigation, both from the practical and the theoretical point of view. In particular, oxidation occurring by a electron transfer mechanism has attracted the most attention. It is generally accepted that side-chain oxidation of an alkylarene (e.g., Ar-CH₃) by an one-electron oxidant (e.g., Ce(IV)) often involves initial oxidation of the alkylarene to a radical cation. The radical cation then undergoes loss of a benzylic proton (called deprotonation or proton transfer), and the resulting radical is further oxidized to a benzylic carboncation, which can be trapped by a nucleophile or solvent present in the solution to lead to final product (Eq. 1-8 → 1-11).
\[
\text{Ar-CH}_3 + \text{Ce(IV)} \rightarrow \text{Ar-CH}_3^{+} + \text{Ce(III)} \tag{1-8}
\]

\[
\text{Ar-CH}_3^{+} \rightarrow \text{H}^{+} + \text{Ar-CH}_2^{-} \tag{1-9}
\]

\[
\text{Ar-CH}_2^{-} + \text{Ce(IV)} \rightarrow \text{Ar-CH}_2^{+} + \text{Ce(III)} \tag{1-10}
\]

\[
\text{Ar-CH}_2^{+} + \text{Nu}^{-} \rightarrow \text{Ar-CH}_2\text{-Nu} \tag{1-11}
\]

While most of substrates chosen for studies on deprotonation reactions of alkylaromatic radical cations are alkylbenzenes, a few of them also come from alkynaphthalenes and alkylanthracenes. The oxidants employed in these studies are mainly higher valence metals or other reagents, such as ceric (IV) ammonium nitrate, peroxydisulfate-Cu(II), tris(phenanthroline) iron(III) complex, etc.. Other radical cation generating methods include anodic oxidation and photochemical oxidation.

**Alkylbenzenes.** Baciocchi, et al.\textsuperscript{48} have extensively studied mechanism of oxidation of alkylbenzenes. The orientation, positional and substrate selectivity in the side-chain oxidation of some alkylbenzenes by Ce(IV) in acetic acid was determined. The reaction was found to be very sensitive to the electronic effects of substituents, a strong accelerating effect being produced by the progressive introduction of methyl groups. Hexamethylbenzene is revealed as ca. $10^5$ fold more reactive then mesitylene.

The relative reactivity of $C_\alpha$-H bonds of methyl, ethyl and isopropyl groups in mono- or $p$-disubstituted benzenes, namely intermolecular or intramolecular TSP (Tertiary, Secondary and Primary) selectivity, was determined and it was found that secondary C-H bond is the most reactive one and tertiary center can be either more or less reactive then the primary one, which was not expected for a free radical chain reaction ($i^{Pr}$

---

21
> Et > Me). This reactivity order may provide a tool to distinguish electron transfer mechanism from hydrogen atom transfer mechanism.¹⁴⁹

The deuterium isotope effect in the side-chain oxidation of alkyl aromatic compounds with Ce(IV) was determined. The results fully confirm the mechanism of the Eq. 1-8 → 1-11 for the reaction of this metal and also show that the slow step of the reaction can change depending on the substrate structure.⁵⁰

Fujita and Fukuzumi⁵¹ in 1993 found that the isopropyl group has no significant stereoelectronic effect on inter- and intramolecular competition in deprotonation from alkylbenzene radical cations in the photoaddition of alkylbenzenes derivatives with 10-methylacridinium ion via photoinduced electron transfer from alkylbenzene derivatives to the singlet excited state of 10-methylacridinium ion, followed by the deprotonation of alkylbenzene radical cations. This result was somewhat controversial to that Schultz, et al.⁵² reported many years ago. Schultz, et al. proposed that a conformation in which the isopropyl group bisects the plane of p-cymene would hinder deprotonation from the tertiary center of the radical cation, although steoroelectronic effects in the gas phase has been shown not to exist by Baciocchi, et al..⁵³

The electronic and stereoelectronic effects of α-substituents on the deprotonation rate from the benzylic position of alkyl aromatic radical cations, \( k(CH_2Z)/k(CH_3) \), has been investigated by determining the intramolecular selectivity in the anodic oxidation in acetic acid of α-Z-substituted p-xylenes.⁵⁴ It has been found that, with the exception of when Z is tert-butyl, the deprotonation rate of p-xylene radical cations is always faster from the CH₂Z group than from the CH₃ group, independently of the electron-donating or electron-
withdrawing nature of Z. The negligible deprotonation rate from \( \text{CH}_2-t\text{-Bu} \) has been ascribed to stereoelectronic effects.

In 1986, Baciocchi, et al. reported substituent effects on intramolecular selectivity and free energy relationships in anodic and metal ion oxidation of 5-X-1,2,3-trimethylbenzenes. In Ce(IV) promoted and electrochemical reactions, very similar substituent effects on the \( k_2/k_1 \) (reactivity of the 2- and 1-methyl group) were observed. In the reactions of Co(OAc)_3 \( k_2/k_1 \) values were much less sensitive to the nature of substituents than former reactions and very close to those determined for the side-chain bromination of the same substrates by NBS.

The rates of deprotonation for a number of \( \alpha \)-substituted \( p \)-methoxytoluene radical cations have also determined by a laser photolysis technique in CH\(_3\)CN.\(^{55}\) The radical cations have been generated from the corresponding neutral substrates ether by biphenyl/9,10-dicyanoanthracene photosensitized oxidation or by reaction with NO\(_3^-\). It has been found that all \( \alpha \)-substituents increase the deprotonation rates, with the rate constant almost reaching diffusion-controlled limit when \( X = \text{CN} \) and the base is NO\(_3^-\). A kinetic study of the side-chain oxidation of \( \alpha \)-substituted 4-methoxytoluenes by potassium 12-tungstocobalt(III)ate in AcOH/H\(_2\)O (55:45) has been carried out by Baciocchi, et al.\(^{56}\) The reaction follow complex kinetics, suggesting that both the electron transfer and the radical cation deprotonation steps affect the reaction rate.

The distribution between nuclear and side-chain substitution in the oxidation of \( m \)-methoxytolulene, 2-methylnaphthalene, mesitylene, and fluorene by Ce(IV) and Co(III) acetate in acetic acid has been determined by Baciocchi, et al.\(^{57}\) Two oxidants exhibit
remarkably different behaviors, the propensity for nuclear substitution being much stronger with Ce(IV) than with Co(OAc)₃. Recently, side-chain fragmentation (C-C and C-H bond) of arylalkylanol radical cations and the role of α- and β-OH groups were studied by Baciocchi, et al.⁵⁸ as well.

Kochi, et al.⁵⁹ also extensively investigated the kinetics and mechanism of oxidation of alkylbenzenes by metal ions. An electron transfer pathway in side-chain substitution of alkyl aromatics under electrophilic conditions was suggested by Kochi in 1974, based on ESR studies of intermediates. Oxidative substitution of methylarenes by tris(phenanthroline)iron(III) complexes proceeds via initial electron transfer to afford benzylic products in excellent yields.⁶⁰ The growth and decay of radical cation ArCH₃⁺ were observed directly by its ESR spectrum. Marcus theory was applied to these organic processes⁶¹ in the endergonic region. The fast rate of proton transfer from various methylbenzene radical cations to a series of substituted pyridine bases are successfully measured in acetonitrile solution.⁶² The deprotonation rate constants were found to range from 3 × 10² to more than 2 × 10⁷ M⁻¹s⁻¹. The relative acidities of these methylbenzene radical cations can be obtained from the Bronsted correlation of the deprotonation rate constants with pyridine strengths and the standard oxidation potentials of the methylarenes.

During the oxidation of methylarenes such as toluene, studies of the proton transfer reaction are complicated by competing nucleophilic attack and coupling reactions. The kinetics of the deprotonation reactions of the radical cations of several methylarenes were studied by DCV and DLSV in acetonitrile by Parker, et al.⁶³ The kinetic data indicate a second order rate law with rate constants of the order of 10⁷M⁻¹s⁻¹ (Eq. 1-12).
The kinetic isotope effect data as well as the apparent negative activation energies suggest a mechanism consisting of reversible dimerization (Eq. 1-13) followed by rate-determining deprotonation (Eq. 1-14).

\[
\text{rate} = k_{\text{app}}[\text{Ar-CH}_3^{+}]^2 \quad (1-12)
\]

\[
2 \text{Ar-CH}_3^{+} = \text{dimer}(2+) \quad (1-13)
\]

\[
\text{dimer}(2+) + B \rightarrow \text{Ar-CH}_3^{+} + \text{Ar-CH}_3 + \text{BH}^{+} \quad (1-14)
\]

A symmetrical dimer dication or a dimeric \(\pi\)-complex are possible structures for the intermediate. The fact that a first-order deprotonation takes place in other types of experiments, i.e., metal-ion oxidation or pulse radiolysis, is a consequence of the large differences in radical cation concentrations and in some cases the more basic medium that the reactions are carried out in.

The oxidation of a variety of alkylbenzenes, (hydroxyalkyl)benzenes, and styrene derivatives by \(S_2O_8^{2-}-Cu^{II}\) in acetic acid and acetonitrile was studied by Walling, et al.\(^64\) \(SO_4^{2-}\) generated from \(S_2O_8^{2-}\) serves as an one-electron oxidant to oxidize arenes to radical cations. One of the interesting results is that oxidation of cyclopropylbenzene in acetic acid yielded 1-phenyl-1-acetoxy-1-cyclopropane as a major product. It suggests that the rate of proton transfer from the radical cation exceeds that of ring opening.\(^65\)

The methods of estimating the \(pK_a\) of an organic radical cation using thermochemical cycles were reported by Arnold, et al.\(^19\) Calculation showed that the toluene radical cation is an extremely strong acid (\(pK_a = -10 \rightarrow -13\)) and the benzene radical cation a moderately strong acid in acetonitrile solution (\(pK_a = -2 \rightarrow -4\)). These estimates indicate that the radical cations of benzene and toluene should deprotonate even
in moderate acidic media if alternative pathways for decay do not exist. The gas phase acidity of several hydrocarbon radical cations was also determined by thermochemical cycles.\textsuperscript{19}

The reactions of the radical cations of methylated benzene derivatives in aqueous solution were studied in detail by Sehested and Holcman.\textsuperscript{66} The rate constants for deprotonation were found to decrease by three orders of magnitude as the number of methyl groups increases from one to five. The rate constants can be correlated with the ionization potential of the parent compound. In neutral solution the reverse reaction to the acid-catalyzed OH adduct conversion occurs and the radical cations react with water to form the OH adduct. In slightly alkaline solution the radical cations of the higher methylated benzenes (n >= 3) react with hydroxide ions forming the OH adduct.

\textbf{Alkynaphthalenes.} Baciocchi, et al.\textsuperscript{67} investigated the reactions of 1-methyl-, 1-ethyl-, and 1-methyl-4-ethynaphthalenes, induced by Ce(IV) in acetic acid. Product analysis showed that the oxidation of 1-ethynaphthalene and 1-methyl-4-ethynaphthalene leads exclusively side-chain substitution products. For oxidation of 1-methynaphthalene, the side-chain substitution products were accompanied by products of nuclear acetoxylation (30\%). The mole ratio of two side-chain oxidation products (methylacetate to ethylacetate) for oxidation of 1-methyl-4-ethynaphthalene was found to be 1.38, from which a C\textsubscript{2}H\textsubscript{5} : CH\textsubscript{3} reactivity ratio of 2 to 1 was calculated. The mechanism for the oxidation of alkynaphthalenes follows those proposed for alkylbenzenes.

\textbf{Alkylanthracenes.} Chemical and biomimetic oxidation of 9,10-dialkylanthracenes in acetonitrile/water was studied by Tolbert, et, al.\textsuperscript{68} Treatment of 9,10-dimethylanthracene (DMA), 9, 10-diethylanthracene (DEA) and 9-ethyl-10-
methylnanthracene (EMA) with tris(phenanthroline)tris(hexafluorophosphate)iron in 10:90
water acetonitrile under argon proceeded cleanly to give > 90% yields of oxidized
products. Formation of these products is readily interpreted as involving the intermediacy
of the dialkylanthracene radical cation, in accord with the works of Kochi, et al. When a
methyl group is present, rapid deprotonation followed by a second one-electron oxidation
and hydration of the resulting cation occurs, provided a suitable proton carrier (H₂O) is
available. With an ethyl group, stereoelectronic effects inhibit deprotonation. Rather,
elimination of ethylene via an unprecedented seven-member transition state was proposed,
facilitated by conversion of a benzhydryl radical to an α-hydroxybenzhydryl radical.
Steroelectronic effects in the deprotonation of alkylarene radical cations were further
investigated by Tolbert, al et. in 1990.⁶⁹ It was confirmed that unlike 9-
methylnanthracenes, which are oxidized by one-electron oxidants to hydroxymethyl
derivatives, 9-ethylanthracenes undergo a facile chemical or biochemical oxidative
elimination of ethylene to yield an anthrone. The rationale for this dramatic selection
between methyl and ethyl reactivity is a stereoelectronic effect on radical cation
deprotonation. For the ethyl group, Cα-H bond is not perpendicular to aromatic ring due
to peri-interactions, and thus inhibits deprotonation. In 1991, Tolbert, et al.⁷⁰ reported
that oxidation of 9-methylnanthracene by pyridine/iodine proceeds mainly through
nucleophilic attack on the intermediate anthracene radical cation rather than deprotonation
and replacement of a methyl proton by trimethylsilyl completely reverses the
regiochemistry. Recently, Guengerich and Tolbert, et al.⁷¹ reported the oxidation of 9-
alkylanthracenes by cytochrome P450 2B1, horseradish peroxidase, and iron
tetraphenylporphine/iodosylbenzene systems. Anaerobic and Aerobic mechanisms were proposed.

The Cu(II)-S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} oxidation of 9-methylanthracene was studied in refluxing CH\textsubscript{3}CN/acedic acid and aqueous CH\textsubscript{3}CN by Camaioni, et al..\textsuperscript{72,73} Side-chain and nuclear oxidation products and the dimeric compound lepidopterene were produced. A mechanism is proposed where the initially formed radical cation undergoes competing proton loss and reversible nucleophile addition reactions to form respectively the anthracenylmethyl radical and nucleophile adduct radicals, which is oxidized by Cu(II) or S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} to yield the corresponding cations that react to form the products (Scheme 1-11).

Scheme 1-11. Two competing reaction pathways of 9-methylanthracene radical cation

The results suggest that nucleophilic addition is faster than proton loss and that it is more reversible in CH\textsubscript{3}CN/HOAc than in CH\textsubscript{3}CN/H\textsubscript{2}O. The Cu(II)-S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} oxidation of 9-acylanthracenes and 9-acyl-10-methylandthracenes was also studied by Camaioni, et al.\textsuperscript{74}
Obviously, proton loss from methyl or formyl groups was not a competing reaction path for these anthracene radical cations in contrast to those benzene radical cations.

1.3 DISSERTATION DESCRIPTION

Radical Cation “Probes”, An Assumption. The fate of a cyclopropyl group incorporated into a substrate participating in a chemical process often provides useful mechanistic information about the importance of radicals and/or radical ions as intermediates along the reaction pathway. Consequently, cyclopropane-containing substrates have frequently been utilized to “probe” for radical cation intermediates in a number of important chemical and biochemical oxidation (Scheme 1-12). For example, in Dr. Castagnoli’s group, MAO oxidation of CpPTP was extensively studied. The cyclopropane ring opening of CpPTP during MAO oxidation may provide some information about the enzymatic oxidation mechanism (SET or HAT).

\[
\begin{align*}
\text{R}^+ & \quad \rightarrow \quad \text{R}^+ \quad \text{Ph} \\
\text{R}^+ & \quad \rightarrow \quad \text{R}^+ \quad \text{Ph}
\end{align*}
\]

Scheme 1-12. Radical cation rearrangement used as “designer probes” for SET
It is frequently assumed that incorporation of a cyclopropyl group into a substrate will result in ring-opened products if a radical cation is an important reactive intermediate in the reaction pathway. A difficulty associated with this approach is that there is surprisingly little actually known about the chemistry of these cyclopropane radical cations.

In earlier work dealing with radical anions generated from cyclopropylketones, it was found that many of the analogous assumptions pertaining to the facility of ring opening of these species were incorrect (Scheme 1-13). Rates of ring opening of these species were shown to be dramatically retarded by phenomena such as delocalization of spin and charge in the ring-closed form, and by stereoelectronic factors.

\[ \text{Scheme 1-13. Free radical and ketyl anion rearrangement} \]

The information regarding the rate of ring opening of cyclopropane-containing radical cations (and the effects substituents on the mechanism on that rate) is somewhat scarce.
To address this issue, we initiated an investigation of the chemistry of radical cations generated from cyclopropylarenes.

**Stereoelectronic Factors, A Hypothesis.** As introduced in 1.2.1, anodic, photochemical and metal ion oxidation of cyclopropylbenzenes all led to cyclopropane ring-opened products. The mechanism was believed to involve initial one-electron oxidation yielding a radical cation, which subsequently underwent cyclopropane ring opening. Obviously, cyclopropylbenzenes can be regarded as radical cation “probes”.

In 1990, it was shown that $S_{N}2$ ring-opening of cyclopropylarenes by bromine atom was sensitive to stereoelectronic factors. For example, whereas the free radical bromination of cyclopropylbenzene and cyclopropynaphthalene led to cyclopropane ring-opened products (1,3-dibromide), the free radical bromination of 9-cyclopropylanthracene and derivatives yielded exclusively hydrogen abstraction products (Scheme 1-14).

![Scheme 1-14 Free radical bromination of cyclopropylarenes](image)
This observed variation in the chemoselectivity of bromination of cyclopropylarenes is attributable to stereoelectronic factors. For 9-cyclopropyranthracene, the cyclopropyl group adopts a perpendicular conformation since the normally preferred bisected conformation is destabilized by unfavorable steric interactions between the peri-hydrogen and cis-hydrogens in cyclopropyl group. However, for cyclopropylbenzene, the cyclopropyl group is essentially freely rotating with a slight preference for the bisected conformation. The lowest energy conformation of 1-cyclopropynaphthalenes is midway between the bisected and the perpendicular (Scheme 1-15).

![Scheme 1-15. Lowest energy conformations of cyclopropylarenes](image)

Since the π-component of the vicinal C₁-C₂ and C₁-C₃ bonds in the bisected conformation is perfectly aligned with the aromatic π-system, ring opening is facilitated by benzylic stabilization in the transition state. In the perpendicular conformation, it is the C-
H bond that is aligned with the aromatic π-system; abstraction of hydrogen by the bromine atom leads to a transition state in which full benzylic stabilization can be realized (Scheme 1-16). Other conformational studies of cyclopropylarenes were reported as well.\textsuperscript{81}

![Scheme 1-16. Stereoelectronic effects on the chemoselectivity of the free radical bromination of cyclopropylarenes](image)

The transition state for the reaction of a cyclopropylarene with a neutral free radical is isoelectronic to that of the reaction of its radical cation with a nucleophile (Ar-\(c\)-C\(_3\)H\(_5\))\(^+\)/X\(^-\) vs. Ar-\(c\)-C\(_3\)H\(_5\)/X\(^-\)). Consequently, it is our hypothesis that the same stereoelectronic factors should pertain to both processes.

**Dissertation Development, Questions.** The dissertation was designed to answer the questions of whether or not the stereoelectronic effect on the reactivity of cyclopropylarene radical cations is important and what other factors will affect this reactivity. The tasks to complete this dissertation are summarized in the following three
Chapter 1. Historical

aspects: 1) Perform electrochemical and chemical oxidations of cyclopropylarenes: What are the products? What is the fate of cyclopropyl group? 2) Examine decay kinetics of these radical cations: Can the mechanism of oxidation be derived by electrochemical methods? 3) Analyze structure and reactivity relationships for these radical cations: Are stereoelectronic factors important in these systems? The main substrates employed in these studies are shown in the Scheme 1-17.

![Scheme 1-17. Substrates used in studies on chemistry of cyclopropylarene radical cations](image)

$X = \text{H, Br, CH}_3$
2.1 INTRODUCTION

The fate of a cyclopropyl group incorporated into a substrate participating in a chemical process often provides useful mechanistic information about the importance of radicals and/or radical ions as intermediates along the reaction pathway. In earlier work, Tanko et al. examined the chemistry of radical anions which undergo ring opening in analogy to the cyclopropylcarbinyl → homoallyl neutral free radical rearrangement, and the suitability of these reactions as “probes” for single electron transfer (SET) (Scheme 1-13). 79

Cyclopropane derivatives are also frequently employed as probes for radical cation intermediates in a number of important chemical and biochemical oxidations. 75,76,77,78 However, information regarding the rate of ring opening of cyclopropane-containing radical cations (and the effect of substituents on that rate) is somewhat scarce. To address this issue, we initiated a study of the chemistry of radical cations generated from cyclopropylarenes.

Dinnocenzo, et al. have shown that ring opening of the cyclopropylbenzene radical cation occurs via a nucleophile-assisted (i.e., S_N2) pathway (Scheme 1-8). 35,37,38,39,41 This process has been well-characterized in terms of its stereochemistry (inversion of configuration at carbon), kinetics (first-order each in radical cation and nucleophile), regiochemistry, and kinetic isotope effects. The rate of ring opening has been found to be
highly sensitive to substituents on the aromatic ring. For a series of substituted
cyclopropylbenzene radical cations, a correlation to $\sigma^+$ was observed ($\rho = +2.2$).

In the series of aromatic hydrocarbons, naphthalene systems occupy some
properties (e.g., ionization potential, stability of radical cations) between those of benzene
systems and anthracene systems. It is our expectation that results from oxidation of
cyclopropynaphthalenes will help us to know more about the chemistry of
cyclopropylarene radical cations.

Molecular mechanics calculations$^{80,105}$ suggest that the lowest energy conformer of
1-cyclopropynaphthalene is in-between a purely bisected and perpendicular conformation
($\theta = 67^\circ$) (Scheme 1-15), which agrees with the X-ray crystal structure of 4-cyclopropyl-
1-naphthalenecarboxylic acid ($\theta = 54^\circ$), a closely related derivative of 1-
cyclopropynaphthalene. The bisected conformation is 1.2 kcal/mol higher in energy, with
1.4 kcal/mol barrier to inter-conversion. The free radical bromination of 1-
cyclopropynaphthalene gave only cyclopropane ring-opened products (Scheme 1-14), but
the rate of this process is diminished due to unfavorable stereoelectronic factors. For 2-
cyclopropynaphthalene, the bisected conformation is preferred and like
cyclopropylbenzene, ring opening predominates. Does this stereoelectronic factor also
hold true for reactivity of cyclopropynaphthalene radical cations?

Anodic nuclear substitution of naphthalenes$^{82}$ have been performed in the presence
of strong nucleophiles such as methoxylation$^{83}$ in CH$_3$OH/KOH, cyanation$^{84}$ in
CH$_3$CN/NaCN, nitrination$^{85}$ in CH$_3$CN/N$_2$O$_4$ and halogenation$^{86}$ in CH$_3$CN/Et$_4$NX. The
mechanism of oxidation is complicated mainly due to oxidation of most strong
nucleophiles prior to naphthalenes. Photochemical oxidation of a number of methyl-
substituted naphthalenes has been studied by means of ESR spectroscopy.\textsuperscript{87} Radical cations and/or dimer radical cations\textsuperscript{88} were detected as reactive intermediates in the reaction.

Electrochemical techniques have been found to be powerful tools to trace follow up reactions of radical ions generated by heterogeneous electron transfer. A number of these studies has been focused on anthracene systems, mainly due to relative stability of these radical cations. In this chapter, the kinetics and mechanism of the follow-up reaction of radical cations generated from 1-cyclopropynaphthalene (1), 1-bromo-4-cyclopropynaphthalene (2) and 2-cyclopropynaphthalene (3) in the presence of methanol are examined electrochemically.

![Molecules](image)

**Voltammetric Methods.** A thorough description of the voltammetric techniques employed in this study and their application to the elucidation of the mechanism of electrode generated intermediates have been reviewed by Saveant\textsuperscript{89} and Parker.\textsuperscript{90} In summary, voltammetric techniques such as cyclic voltammetry, derivative cyclic voltammetry (CV, DCV) or linear sweep voltammetry (LSV) permit assignment of the rate law for the decay of species generated (reversibly) by heterogeneous electron transfer (Scheme 2-1), where A represents the neutral substrate, B the radical cation, and X
another chemical entity in solution which may be involved in the reaction (e.g.,
nucleophile).

\[
\begin{array}{ccc}
A & \rightarrow & B + e^- \\
\text{a A} & + & \text{b B} + \text{x X} \rightarrow & \text{k product(s)} \\
\end{array}
\]

\[
\frac{-d[B]}{dt} = k [A]^a [B]^b [X]^x
\]

Scheme 2-1. Rate law expression for decay of radical cation B

In cases where no reverse wave is observed in the cyclic voltammogram, linear
sweep voltammetry (LSV) is a powerful technique for studying the follow-up chemistry of
the electrogenerated intermediate. Put briefly, the observed variation in the forward peak
potential (E_p) as a function of sweep rate v, substrate concentration [A], and auxiliary
reagent (nucleophile) concentration [X] can be related to the individual reaction order in
A, B, X according to Eq. 2-1, 2-2, 2-3.

\[
\frac{\partial E_p}{\partial \log(\nu)} = \left[\frac{1}{1/(b+1)}\right]\log(RT/nF) \quad (2-1)
\]

\[
\frac{\partial E_p}{\partial \log([A])} = -[(a + b - 1)/(b + 1)]\log(RT/nF) \quad (2-2)
\]

\[
\frac{\partial E_p}{\partial \log([X])} = -[x/(b + 1)]\log(RT/nF) \quad (2-3)
\]

When a reverse wave is observed, cyclic and derivative cyclic voltammetry (CV,
DCV) and the “reaction order approach” advocated by Parker, et al.\textsuperscript{90} are applicable. The
reaction order approach provides a means of assessing the rate law for radical ion decay
by observing the variation of the cathodic to anodic derivative peak current ratio (I_c/I_a)
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

as a function of \([A]\), \([X]\), and \(v\). A plot of \(\log v_c\) vs. \([A]\) yields a straight line whose slope is related to the combined reaction order in \(A\) and \(B\), named \(R_{AB}\) according to Eq. 2-4, where \(v_c\) represents the sweep rate needed to keep the derivative current ratio at a constant value (typically 0.5). Similarly, \(R_X\) is the reaction order of the auxiliary reagent according to Eq. 2-5.

\[
R_{AB} = a + b = \frac{\partial \log(v_c)}{\partial \log[A]} + 1 \quad (2-4)
\]

\[
R_X = x = \frac{\partial \log(v_c)}{\partial \log[X]} \quad (2-5)
\]

Table 2-1 showed some typical theoretical LSV and CV (or DCV) responses for corresponding rate law of radical cation decay according to the published works.\(^{90}\)

Table 2-1 Theoretical LSV and CV (or DCV) responses for rate law of decay of radical cation generated (reversibly) by heterogeneous electron transfer (25 °C)

<table>
<thead>
<tr>
<th>rate law</th>
<th>LSV (\partial E_p/\partial \log v)</th>
<th>LSV (\partial E_p/\partial \log [A])</th>
<th>LSV (\partial E_p/\partial \log [X])</th>
<th>CV (or DCV) (\partial \log v_c/\partial \log [A])</th>
<th>CV (or DCV) (\partial \log v_c/\partial \log [X])</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k[B])</td>
<td>29.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(k[B][X])</td>
<td>29.6</td>
<td>0</td>
<td>-29.6</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>(k[B][A])</td>
<td>29.6</td>
<td>-29.6</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(k[A][B][X])</td>
<td>29.6</td>
<td>-29.6</td>
<td>-29.6</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(k[B]^2)</td>
<td>19.7</td>
<td>-19.7</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(k[B]^2[X])</td>
<td>19.7</td>
<td>-19.7</td>
<td>-19.7</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(k[B]^2[X] / [A])</td>
<td>19.7</td>
<td>0</td>
<td>-19.7</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
2.2 RESULTS AND DISCUSSION

2.2.1 Kinetic Analysis from Voltammetry

Radical cations generated from 1, 2, and 3 in the presence of methanol were studied electrochemically. Voltammetric techniques such as CV, DCV or LSV were employed to determine the rate law for the decay of 1\(^{+}\), 2\(^{+}\), and 3\(^{+}\). The results are summarized below.

1-Cyclopropynaphthalene (1). The cyclic voltammogram of 1 in CH\(_3\)CN is characterized by an initial oxidation wave (E\(_p\) = \~1130 mV at 400 mV/sec) and continuous indistinguishable oxidation waves located at more positive potentials (Figure 2-1). Addition of methanol does not shift the position (i.e., peak potential) of the initial oxidation wave, but does seem to affect those at more positive potentials.

Figure 2-1. Cyclic voltammogram of 1 in CH\(_3\)CN (0.5 M LiBF\(_4\), 1.14 \times 10\(^{-3}\) M 1, \(v = 400\) mV/sec)
Because the initial wave is irreversible, LSV was employed to study the decay of \( 1^+ \). The peak potential (\( E_P \)) of the initial oxidation wave was found to vary as a function of both sweeprate (\( v \)) and substrate concentration ([A]), but was independent of methanol concentration ([X]). The results are summarized in Figures 2-2→2-13 and Table 2-2. These observations are in excellent agreement with a second-order rate law for radical cation decay (Eq. 2-6),

\[-d[1^+]/dt = k[1^+]^2\]  

(2-6)

for which the theoretical response is \( \partial E_P/\partial \log(v) = 19.7 \), \( \partial E_P/\partial \log([A]) = -19.7 \), and \( \partial E_P/\partial \log([X]) = 0 \) (all in units of mV/decade, where \( A = \) substrate and \( X = \text{CH}_3\text{OH} \)).

<table>
<thead>
<tr>
<th>electrolyte</th>
<th>( \partial E_P/\partial \log(v)^a )</th>
<th>( \partial E_P/\partial \log([1]^b )</th>
<th>( \partial E_P/\partial \log([\text{CH}_3\text{OH}]^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M LiBF(_4)</td>
<td>19.5 ± 0.3 (1.19)</td>
<td>-18.2 ± 2.9 (1.19→9.52)</td>
<td>-0.34 ± 0.57 (1.19)</td>
</tr>
<tr>
<td></td>
<td>18.8 ± 1.0 (2.26)</td>
<td>-23.1 ± 1.3 (0.476→9.52)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22.2 ± 0.9 (9.52)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 M LiClO(_4)</td>
<td>18.7 ± 0.3 (0.595)</td>
<td>-20.9 ± 2.8 (0.595→9.52)</td>
<td>1.50 ± 1.07 (6.85)</td>
</tr>
<tr>
<td></td>
<td>20.0 ± 0.9 (9.52)</td>
<td>-19.3 ± 1.0 (1.67→12.9)</td>
<td>-0.20 ± 1.11 (1.25)</td>
</tr>
</tbody>
</table>

\(^a\) 0.5 M \text{CH}_3\text{OH}, \( v = 100→3000 \text{ mV/sec} \), [1] (mM) appears in parentheses;

\(^b\) 0.5 M \text{CH}_3\text{OH}, \( v = 400 \text{ mV/sec} \), [1] (mM) range appears in parentheses;

\(^c\) 0.025→0.5 M \text{CH}_3\text{OH}, \( v = 400 \text{ mV/sec} \), [1] (mM) appears in parentheses.
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

Figure 2-2. LSV analysis of 1, \( \frac{\partial E_p}{\partial \log(v)} \). (0.5 M LiBF\(_4\), 0.5 M CH\(_3\)OH, 1.19 \times 10^{-3} \text{ M} 1, v = 100\rightarrow3000 \text{ mV/sec})

\[
y = 19.487x + 1079 \\
R^2 = 0.9991
\]

Figure 2-3. LSV analysis of 1, \( \frac{\partial E_p}{\partial \log[1]} \). (0.5 M LiBF\(_4\), 0.5 M CH\(_3\)OH, 1.19\rightarrow9.52 \times 10^{-3} \text{ M} 1, v = 400 \text{ mV/sec})

\[
y = -18.151x + 1075 \\
R^2 = 0.9288
\]
Figure 2-4. LSV analysis of 1, $\partial E_p/\partial \log([\text{CH}_3\text{OH}])$. (0.5 M LiBF$_4$, 0.0125→0.5 M CH$_3$OH, 1.19×10$^{-3}$ M 1, $\nu = 400$ mV/sec)

\[
y = -0.3376x + 1130.6 \\
R^2 = 0.1038
\]

Figure 2-5. LSV analysis of 1, $\partial E_p/\partial \log(\nu)$. (0.5 M LiBF$_4$, 0.5 M CH$_3$OH, 2.26×10$^{-3}$ M 1, $\nu = 100$→3000 mV/sec)

\[
y = 18.754x + 1074.3 \\
R^2 = 0.9898
\]
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

Figure 2-6. LSV analysis of $1$, $\partial E_p/\partial \log(\nu)$. (0.5 M LiBF$_4$, 0.5 M CH$_3$OH, $9.52 \times 10^{-3}$ M $1$, $\nu = 100\rightarrow3000$ mV/sec)

$$y = 22.194x + 1057.3$$
$$R^2 = 0.9941$$

Figure 2-7. LSV analysis of $1$, $\partial E_p/\partial \log[1]$. (0.5 M LiBF$_4$, 0.5 M CH$_3$OH, $0.476\rightarrow9.52 \times 10^{-3}$ M $1$, $\nu = 400$ mV/sec)

$$y = -23.098x + 1060.9$$
$$R^2 = 0.9825$$
Figure 2-8. LSV analysis of 1, $\partial E_p/\partial \log [1]$. (0.5 M LiClO$_4$, 0.5 M CH$_3$OH, 0.595→9.52 × 10$^{-3}$ M 1, $v = 400$ mV/sec)

\[ y = -20.909x + 1056.4 \]
\[ R^2 = 0.9183 \]

Figure 2-9. LSV analysis of 1, $\partial E_p/\partial \log (v)$. (0.5 M LiClO$_4$, 0.5 M CH$_3$OH, 5.95 × 10$^{-3}$ M 1, $v = 100$→3000 mV/sec)

\[ y = 18.71x + 1076.8 \]
\[ R^2 = 0.9992 \]
Figure 2-10. LSV analysis of 1, $\partial E_p/\partial \log (v)$. (0.5 M LiClO$_4$, 0.5 M CH$_3$OH, 9.52 $\times$ $10^{-3}$ M 1, $v = 100 \rightarrow 3000$ mV/sec)

$$y = 19.977x + 1047.5$$
$$R^2 = 0.9918$$

Figure 2-11. LSV analysis of 1, $\partial E_p/\partial \log$[CH$_3$OH]. (0.5 M LiClO$_4$, 0.025 $\rightarrow$ 0.5 M CH$_3$OH, 6.845 $\times$ $10^{-3}$ M 1, $v = 400$ mV/sec)

$$y = 1.5039x + 1109.5$$
$$R^2 = 0.4956$$
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

Figure 2-12. LSV analysis of 1, $\partial E_p/\partial \log[\text{CH}_3\text{OH}]$. (0.5 M LiClO$_4$, 0.025→0.5 M CH$_3$OH, 1.25 × $10^{-3}$ M 1, $v = 400$ mV/sec)

$y = -0.1972x + 1113.5$
$R^2 = 0.0156$

Figure 2-13. LSV analysis of 1, $\partial E_p/\partial \log[1]$. (0.5 M LiClO$_4$, 0.5 M CH$_3$OH, 1.67→12.9 × $10^{-3}$ M 1, $v = 400$ mV/sec)

$y = -19.297x + 1070.9$
$R^2 = 0.9942$
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

1-Bromo-4-cyclopropynaphthalene (2). The cyclic voltammogram of 2 in CH₃CN is characterized by an initial oxidation wave (Eₚ = ~1245 mV, at 400 mV/sec) and other subsequent oxidation waves located at much more positive potentials (Figure 2-14). In the presence of methanol, the waves at more positive potentials appear to shift in the negative direction, but the initial oxidation wave is not affected.

Figure 2-14. Cyclic voltammogram of 2 in CH₃CN (0.5 M LiBF₄, 2.36 × 10⁻³ M 2, ν = 400 mV/s)

As was observed for 1, the initial oxidation wave of 2 in CH₃CN is irreversible and thus, LSV is applicable. Eₚ was found to vary as a function of both sweep rate and substrate concentration, but was independent of methanol concentration. The LSV results for the electrochemical oxidation of 2 appear in Figures 2-15→2-31 and Table 2-3, and are also consistent with a mechanism that is second order in radical cation and zero order in
methanol (Eq. 2-7). Different supporting electrolytes and solvents do not alter the observed rate law.

\[-d[2^+] / dt = k[2^+]^2\]  \hspace{1cm} (2-7)

Table 2-3  Observed LSV response for the electrochemical oxidation of 2 in several solvent/electrolyte combinations

<table>
<thead>
<tr>
<th>electrolyte/solvent</th>
<th>$\partial E_p / \partial \log(v)^a$</th>
<th>$\partial E_p / \partial \log[2]^b$</th>
<th>$\partial E_p / \partial \log[\text{CH}_3\text{OH}]^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M LiBF$_4$/CH$_3$CN</td>
<td>19.5 ± 0.9 (6.79) 19.4 ± 0.7 (2.36)</td>
<td>-20.9 ± 2.8 (2.36→9.07) -21.5 ± 2.8 (1.59→13.8)</td>
<td>-1.2 ± 0.7 (6.79)</td>
</tr>
<tr>
<td>0.5 M LiClO$_4$/CH$_3$CN</td>
<td>20.3 ± 0.4 (2.36) 20.7 ± 0.6 (9.44)</td>
<td>-19.5 ± 1.0 (0.59→9.44) -0.27 ± 0.6 (5.67)</td>
<td></td>
</tr>
<tr>
<td>0.25 M $^\text{t}\text{Bu}_4\text{NPF}_6$/CH$_3$CN</td>
<td>20.7 ± 0.5 (1.18) 20.8 ± 0.4 (9.44)</td>
<td>-18.1 ± 1.1 (1.18→9.44) -5.9 ± 1.0 (1.18)</td>
<td></td>
</tr>
<tr>
<td>0.25 M $^\text{t}\text{Bu}_4\text{NPF}_6$/1:1CH$_3$CN:CH$_2$Cl$_2$</td>
<td>19.3 ± 0.4 (2.96) 21.1 ± 0.4 (9.44)</td>
<td>-17.4 ± 2.0 (1.18→9.44) -0.64 ± 0.5 (2.36)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 0.5 M CH$_3$OH, v = 100→6000mV/s, [2] (mM) appears in parentheses;

$^b$ 0.5 M CH$_3$OH, v = 400 mV/sec, [2] (mM) range appears in parentheses;

$^c$ 0.025→0.5 M CH$_3$OH, v = 400 mV/sec, [2] (mM) appears in parentheses.
Figure 2-15. LSV analysis of 2, $\partial E_p/\partial \log([\text{CH}_3\text{OH}])$. (0.5 M LiBF$_4$, 0.025→0.5 M \text{CH}_3\text{OH}, 6.79 \times 10^{-3} \text{M} 2, v = 400 \text{ mV/sec})

![Graph showing LSV analysis of 2, $\partial E_p/\partial \log([\text{CH}_3\text{OH}])$.]

$y = -1.2086x + 1231.3$
$R^2 = 0.4987$

Figure 2-16. LSV analysis of 2, $\partial E_p/\partial \log(v)$. (0.5 M LiBF$_4$, 0.5 M \text{CH}_3\text{OH}, 6.79 \times 10^{-3} \text{M} 2, v = 100→6000 \text{ mV/sec})

![Graph showing LSV analysis of 2, $\partial E_p/\partial \log(v)$.]

$y = 19.48x + 1179$
$R^2 = 0.9888$
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

Figure 2-17. LSV analysis of 2, $\partial E_p/\partial \log[\text{CH}_3\text{OH}]$. (0.5 M LiClO$_4$, 0.025→0.5 M CH$_3$OH, $5.67 \times 10^{-3}$ M $\text{H}_2$, $v = 400$ mV/sec)

\[ y = -0.2685x + 1218.5 \]
\[ R^2 = 0.0895 \]

Figure 2-18. LSV analysis of 2, $\partial E_p/\partial \log(v)$. (0.5 M LiBF$_4$, 0.5 M CH$_3$OH, $2.36 \times 10^{-3}$ M 2, $v = 100$→6000 mV/sec)

\[ y = 19.368x + 1189.3 \]
\[ R^2 = 0.9944 \]
Figure 2-19. LSV analysis of 2, $\partial E_p/\partial \log [2]$. (0.5 M LiBF$_4$, 0.5 M CH$_3$OH, $2.36 \rightarrow 9.07 \times 10^{-3}$ M 2, $v = 400$ mV/sec)

$$y = -20.935x + 1184.3$$
$$R^2 = 0.9662$$

Figure 2-20. LSV analysis of 2, $\partial E_p/\partial \log [2]$. (0.5 M LiBF$_4$, 0.5 M CH$_3$OH, $1.59 \rightarrow 13.8 \times 10^{-3}$ M 2, $v = 400$ mV/sec)

$$y = -21.476x + 1186.5$$
$$R^2 = 0.9373$$
Figure 2-21. LSV analysis of $2, \partial E_p/\partial \log[2]$. (0.5 M LiClO$_4$, 0.5 M CH$_3$OH, 0.59→9.44×10$^{-3}$ M $2, v = 400$ mV/sec)

Figure 2-22. LSV analysis of $2, \partial E_p/\partial \log(v)$. (0.5 M LiClO$_4$, 0.5 M CH$_3$OH, 2.36×10$^{-3}$ M $2, v = 100$→6000 mV/sec)
Figure 2-23. LSV analysis of 2, $\partial E_P/\partial \log(\nu)$. (0.5 M LiClO$_4$, 0.5 M CH$_3$OH, $9.44 \times 10^{-3}$ M 2, $\nu = 100 \rightarrow 6000$ mV/sec)

$y = 20.694x + 1159.2$

$R^2 = 0.996$

Figure 2-24. LSV analysis of 2, $\partial E_P/\partial \log[\text{CH}_3\text{OH}]$. (0.25 M $^8\text{Bu}_4\text{NPF}_6$, 0.025→0.25 M CH$_3$OH, $1.18 \times 10^{-3}$ M 2, $\nu = 400$ mV/sec)

$y = -5.8668x + 1269$

$R^2 = 0.9493$
Figure 2-25. LSV analysis of $2$, $\partial E_p/\partial \log[2]$. (0.25 M $^{n}$Bu$_4$NPF$_6$, 0.25 M CH$_3$OH, $1.18 \rightarrow 9.44 \times 10^{-3}$ M $2$, $v = 400$ mV/sec)

\[ y = -18.081x + 1219.4 \]
\[ R^2 = 0.9889 \]

Figure 2-26. LSV analysis of $2$, $\partial E_p/\partial \log(v)$. (0.25 M $^{n}$Bu$_4$NPF$_6$, 0.25 M CH$_3$OH, $1.18 \times 10^{-3}$ M $2$, $v = 100 \rightarrow 3000$ mV/sec)

\[ y = 20.645x + 1216.5 \]
\[ R^2 = 0.9981 \]
Figure 2-27. LSV analysis of 2, \( \partial E_p / \partial \log(v) \). (0.25 M \( \text{Bu}_4\text{NPF}_6 \), 0.25 M CH\(_3\)OH, 9.44 \times 10^{-3} \text{ M 2}, v = 100\rightarrow3000 \text{ mV/sec})

![Graph 1](image1)

\[ y = 20.844x + 1207 \]
\[ R^2 = 0.9989 \]

Figure 2-28. LSV analysis of 2, \( \partial E_p / \partial \log(v) \). (0.25 M \( \text{Bu}_4\text{NPF}_6 \), CH\(_2\)Cl\(_2\)/CH\(_3\)CN (1:1), 2.36 \times 10^{-3} \text{ M 2}, v = 100\rightarrow6000 \text{ mV/sec})

![Graph 2](image2)

\[ y = 19.308x + 1264.7 \]
\[ R^2 = 0.998 \]
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

Figure 2-29. LSV analysis of 2, $\partial E_p / \partial \log([\text{CH}_3\text{OH}])$. (0.25 M $^6$Bu$_4$NPF$_6$, 0.0125→0.125 M CH$_3$OH, CH$_2$Cl$_2$/CH$_3$CN (1:1), 2.36 × 10$^{-3}$ M 2, $v = 400$ mV/sec)

$$y = -0.6381x + 1310.6$$
$$R^2 = 0.446$$

Figure 2-30. LSV analysis of 2, $\partial E_p / \partial \log([2])$. (0.25 M $^6$Bu$_4$NPF$_6$, 0.25 M CH$_3$OH, CH$_2$Cl$_2$/CH$_3$CN (1:1), 1.18→9.44 × 10$^{-3}$ M 2, $v = 400$ mV/sec)

$$y = -17.363x + 1265.3$$
$$R^2 = 0.9617$$
When CH$_2$Cl$_2$ is used as solvent, the cyclic voltammogram of 2 changes significantly. The initial oxidation wave shifts to a more positive potential ($\Delta E_p \approx 130$ mV) and begins to merge with the subsequent oxidation waves (Figure 2-32, curve a).

Unlike in CH$_3$CN, at higher sweeps rates in CH$_2$Cl$_2$, the initial wave of 2 becomes reversible (Figure 2-32, curve b) indicating that 2$^+$ is longer-lived in CH$_2$Cl$_2$ than in CH$_3$CN. The DCV “reaction order approach” was employed to study decay of 2$^+$ (Figures 2-33 ~ 35 and Table 2-4). The results obtained from this analysis are also consistent with a bimolecular decay of 2$^+$ in CH$_2$Cl$_2$.  

$91$
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

Figure 2-32  Cyclic voltammogram of \( \text{2} \) in \( \text{CH}_2\text{Cl}_2 \) (0.5 M \( \text{Bu}_4\text{NPF}_6 \), \( 2.36 \times 10^{-3} \text{ M} \) \( \text{2} \))

![Cyclic voltammogram](image)

a) 100 mV/s (current x 8)

b) 20,000 mV/s

Table 2-4. Observed DCV response for the electrochemical oxidation of \( \text{2} \) in \( \text{CH}_2\text{Cl}_2 \) and in the presence of \( \text{CH}_3\text{CN} \) or \( \text{CH}_3\text{OH} \)

<table>
<thead>
<tr>
<th>( \partial \log(\nu_c) / \partial \log[2] )</th>
<th>( \partial \log(\nu_c) / \partial \log[X] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.04 ± 0.04(^a)</td>
<td>0.30 ± 0.01 (X = CH(_3)OH)(^b)</td>
</tr>
<tr>
<td></td>
<td>0.27 ± 0.01 (X = CH(_3)CN)(^c)</td>
</tr>
</tbody>
</table>

\(^a\) 0.25 M \( \text{Bu}_4\text{NPF}_6 \), 0.00059→0.0059 M \( \text{2} \);  

\(^b\) 0.5 M \( \text{Bu}_4\text{NPF}_6 \), 0.00236 M \( \text{2} \), 0.125→1.25 M CH\(_3\)OH;  

\(^c\) 0.25 M \( \text{Bu}_4\text{NPF}_6 \), 0.00177 M \( \text{2} \), 0.0958→3.83 M CH\(_3\)CN.
Figure 2-33. DCV analysis of 2, $\partial \log(v_c)/\partial \log([2])$. (0.25 M $^6$Bu$_4$NPF$_6$-CH$_2$Cl$_2$, 0.59→5.9 $\times 10^{-3}$ M 2, $v = 200→8000$ mV/sec, $I'_{pc}/I'_{pa} = 0.6$)

$y = 1.0448x + 5.8677$

$R^2 = 0.9984$

Figure 2-34. DCV analysis of 2, $\partial \log(v_c)/\partial \log([\text{CH}_3\text{OH}])$. (0.5 M $^6$Bu$_4$NPF$_6$-CH$_2$Cl$_2$, 0.125→1.325 M CH$_3$OH, 2.36 $\times 10^{-3}$ M 2, $v = 5→50$ V/sec, $I'_{pc}/I'_{pa} = 0.7$)

$y = 0.2996x + 4.4024$

$R^2 = 0.9989$
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

Figure 2-35. DCV analysis of 2, \( \partial \log(v_c)/\partial \log[\text{CH}_3\text{CN}] \). (0.25 M \( \text{Bu}_4\text{NPF}_6 - \text{CH}_2\text{Cl}_2 \), 0.985 \( \rightarrow \) 3.83 M CH–CN, 1.77 \( \times \) 10\(^{-3}\) M 2, \( v = 100 \rightarrow 8000 \) mV/sec, \( \Gamma'_{pc}/\Gamma'_{pa} = 0.6 \))

Addition of CH–CN or CH–OH (to CH–Cl\(_2\) solvent) slightly affects the cathodic to anodic derivative current ratio (\( \Gamma'_{pc}/\Gamma'_{pa} \)), resulting in an apparent reaction order of ca. 0.3. However, this small change in the derivative current ratio, coupled with the LSV results which show no change in \( E_p \) with CH–OH concentration (in CH–CN or 1:1 CH–CN:CH–Cl\(_2\) solvents) suggest these observations are more the result of a solvent effect on the rate constant for dimerization (or disproportionation) of \( 2^+ \), rather than any significant participation of either CH–OH or CH–CN in the decay mechanism.

Because the rate law for the decay of \( 2^+ \) is now known, it becomes possible to calculate the rate constant for dimerization of \( 2^+ \) in CH–Cl\(_2\). DCV was employed to obtain the experimental derivative peak current ratio (\( \Gamma'_{pc}/\Gamma'_{pa} \)) at various sweeprates for a
given concentration of substrate. The data in the region of $I'_p/I'_pa = 0.4 \sim 0.8$ were used in this analysis. Theoretical working curve was generated via digital simulation (Figure 2-36). Equations for $k_{\text{dim}}$ from this working curve at 298 K is $k_{\text{dim}} = 4.0v_{0.7}/C_A$, $k_{\text{dim}} = 6.8v_{0.6}/C_A$, $k_{\text{dim}} = 12.5v_{0.5}/C_A$, where $v_c$ in V/s, $C_A$ in M. The rate constant for dimerization of $2^+$ is found to be $3.9 (\pm 0.2) \times 10^3$ M$^{-1}$s$^{-1}$ in CH$_2$Cl$_2$. Similarly, rate constants for dimerization of $2^+$ in CH$_2$Cl$_2$ at various concentrations of CH$_3$CN or CH$_3$OH were obtained (Table 2-5). With an increase of CH$_3$CN or CH$_3$OH concentration, the rate constants for dimerization of $2^+$ increase.

Figure 2-36. Dimensionless working curve for EC$_{\text{dim}}$ mechanism ( A - e$^-$ = B, 2B = C, rate = $k_{\text{dim}}C_A^{-2}$)
Table 2-5. Rate constant for dimerization of 2+ (CH₂Cl₂ solvent mixed with varying amounts of CH₃OH or CH₃CN)

<table>
<thead>
<tr>
<th>[CH₃CN] (M)</th>
<th>v₀.₆ (mV/sec) (Cₐ = 0.00177 M)</th>
<th>kₐₐₐᵢₐ (M⁻¹s⁻¹)</th>
<th>CₐₐₐMeOH (M)</th>
<th>v₀.₇ (mV/sec) (Cₐ = 0.00236 M)</th>
<th>kₐₐₐₐₐ (M⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3900</td>
<td>0.125</td>
<td>13500</td>
<td>22900</td>
<td></td>
</tr>
<tr>
<td>0.0958</td>
<td>1670</td>
<td>6400</td>
<td>0.75</td>
<td>23500</td>
<td>39800</td>
</tr>
<tr>
<td>0.192</td>
<td>2000</td>
<td>7700</td>
<td>1.38</td>
<td>27500</td>
<td>46600</td>
</tr>
<tr>
<td>0.383</td>
<td>2330</td>
<td>8900</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.766</td>
<td>2890</td>
<td>11100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.92</td>
<td>3610</td>
<td>13800</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.83</td>
<td>4670</td>
<td>17900</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2-Cyclopropylnaphthalene (3). The cyclic voltammogram of 3 in CH₃CN is similar to that of 1, characterized by an initial oxidation wave (Eₚ = ~1157 mV at 400 mV/sec) which is not affected by the addition of methanol (Figure 2-37).

Figure 2-37. Cyclic voltammogram of 3 in CH₃CN (0.5 M LiClO₄, 1.19 × 10⁻³ M 3, v = 400 mV/s)
Because the initial oxidation wave is completely irreversible at sweeprates under 8000 mV/sec in CH$_3$CN, LSV was used to study the decay of 3$^+$. Figures 2-38→2-48 and Table 2-6 summarize the LSV results for the electrochemical oxidation of 3. As was found for 1$^+$ and 2$^+$, the decay of 3$^+$ is second order in radical cation and zero order in methanol (Eq. 2-8):


(2-8)

Table 2-6. Observed LSV response for the electrochemical oxidation of 3 in CH$_3$CN

<table>
<thead>
<tr>
<th>electrolytes</th>
<th>$\partial E_p / \partial \log(v)^a$</th>
<th>$\partial E_p / \partial \log[3]^b$</th>
<th>$\partial E_p / \partial \log[\text{CH}_3\text{OH}]^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M LiBF$_4$</td>
<td>16.8 ± 1.0 (1.2)</td>
<td>-20.5 ± 3.0 (1.19→7.14)</td>
<td>-0.54 ± 0.33 (1.2)</td>
</tr>
<tr>
<td></td>
<td>18.4 ± 0.5 (7.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 M LiClO$_4$</td>
<td>18.6 ± 0.4 (1.2)</td>
<td>-22.0 ± 0.6 (1.19→7.14)</td>
<td>1.19 ± 0.37 (10)</td>
</tr>
<tr>
<td></td>
<td>20.9 ± 0.4 (7.1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$0.5 M CH$_3$OH, $v = 100$→3000 mV/s, [3] (mM) appears in parentheses;

$^b$0.5 M CH$_3$OH, $v = 400$ mV/sec, [3] (mM) range appears in parentheses;

$^c$0.025→0.5 M CH$_3$OH, $v = 400$ mV/sec, [3] (mM) appears in parentheses.
Figure 2-38. LSV analysis of 3, $\partial E_p/\partial \log [3]$. (0.5 M LiBF$_4$, 0.5 M CH$_3$OH, 1.19→7.14 × $10^{-3}$ M 3, $v = 400$ mV/sec)

![Graph showing LSV analysis of 3, $\partial E_p/\partial \log [3]$.](image)

$y = -20.457x + 1117$

$R^2 = 0.9391$

Figure 2-39. LSV analysis of 3, $\partial E_p/\partial \log (v)$. (0.5 M LiBF$_4$, 0.5 M CH$_3$OH, 1.19 × $10^{-3}$ M 3, $v = 200$→6000 mV/sec)

![Graph showing LSV analysis of 3, $\partial E_p/\partial \log (v)$.](image)

$y = 16.833x + 1133.7$

$R^2 = 0.9847$
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

Figure 2-40. LSV analysis of 3, $\partial E_p/\partial \log(v)$. (0.5 M LiBF$_4$, 0.5 M CH$_3$OH, 7.14 x 10$^{-3}$ M 3, $v = 200 \rightarrow 6000$ mV/sec)

$y = 18.39x + 1118.3$
$R^2 = 0.9965$

Figure 2-42. LSV analysis of 3, $\partial E_p/\partial \log([CH_3OH])$. (0.5 M LiBF$_4$, 0.0125 $\rightarrow$ 0.5 M CH$_3$OH, 1.19 x 10$^{-3}$ M 3, $v = 400$ mV/sec)

$y = -0.5369x + 1178.1$
$R^2 = 0.4027$
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

Figure 2-43. LSV analysis of 3, $\partial E_p/\partial \log[3]$. (0.5 M LiClO$_4$, 0.5 M CH$_3$OH, 1.19→7.14 $\times 10^{-3}$ M 3, $v = 400$ mV/sec)

$y = -21.963x + 1094$

$R^2 = 0.9987$

Figure 2-44. LSV analysis of 3, $\partial E_p/\partial \log(v)$. (0.5 M LiClO$_4$, 0.5 M CH$_3$OH, 7.1 $\times 10^{-3}$ M 3, $v = 200$→3000 mV/sec)

$y = 20.943x + 1093.2$

$R^2 = 0.9986$
Figure 2-45. LSV analysis of $3$, $\partial E_P/\partial \log(v)$. (0.5 M LiClO$_4$, 0.5 M CH$_3$OH, $1.2 \times 10^{-3}$ M $3$, $v = 200 \rightarrow 3000$ mV/sec)

\[ y = 18.618x + 1116.5 \]
\[ R^2 = 0.9986 \]

Figure 2-46. LSV analysis of $3$, $\partial E_P/\partial \log[\text{CH}_3\text{OH}]$. (0.5 M LiClO$_4$, 0.025 $\rightarrow$ 0.5 M CH$_3$OH, $1.0 \times 10^{-3}$ M $3$, $v = 400$ mV/sec)

\[ y = 1.1909x + 1146.6 \]
\[ R^2 = 0.7747 \]
2.2.2 Product Analysis from Preparative Electrolysis

Constant current electrolyses of 1, 2 and 3 were conducted in CH$_3$CN/CH$_3$OH with 0.1 M LiClO$_4$ as the supporting electrolyte. Ultrasound was employed to increase mass transfer efficiency during electrolysis. GC was used to monitor electrolytic progress.

**1-Cyclopropynaphthalene (1).** The anodic oxidation of 1 in CH$_3$CN/CH$_3$OH mainly produces cyclopropane ring-opened products, 1-(1,3-dimethoxypropyl)-naphthalene (4) and dimer 4,4’-di(1,3-dimethoxypropyl)-1,1’-binaphthalene (5, Scheme 2-2). In a typical run, 17.4% of 4, 26.3% of 5, and 7.5% of 1 were recovered after the transfer of 3.5 equivalents of electrons. Minor product 6 was detected by GC/MS, but not isolated.

Scheme 2-2 Anodic oxidation of 1 in CH$_3$CN/CH$_3$OH
1-Bromo-4-cyclopropynaphthalene (2). Oxidation of 2 yields exclusively cyclopropane ring-opened 1-bromo-4-(1,3-dimethoxypropyl)-naphthalene (7), in 80% yield after the transfer of two equivalents of electrons (Scheme 2-3). Some 2 (13.2%) was also recovered.

Scheme 2-3. Anodic oxidation of 2 in CH₃CN/CH₃OH

2-Cyclopropynaphthalene (3). The anodic oxidation of 3 in CH₃CN/CH₃OH yields, after the transfer of two equivalents of electrons, 2-(1,3-dimethoxypropyl)-naphthalene (8) and dimer 2, 2’-dicyclopropyl-1,1’-binaphthalene (9) as major products. The isolated yield of 8 and 9 was 16.2% and 17.5%, respectively (Scheme 2-4). In addition, a large amount of starting material (34.1%) was recovered.
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

Scheme 2-4. Anodic oxidation of 3 in CH$_3$CN/CH$_3$OH

2.2.3 Reaction Mechanism

**Oxidation of 1-cyclopropynaphthalene (1).** LSV analyses for 1 reveal that decay of 1$^+$ in CH$_3$CN is second-order in radical cation and zero order in methanol. Preparative electrolysis of 1 produces the cyclopropane ring-opened (1,3-dimethoxypropyl) products. These results suggest that attack of methanol at the cyclopropane ring must occur after the rate determining step.

The second order rate law and appearance of dimers 5 and 6 as products are consistent with a radical cation dimerization mechanism (Scheme 2-5). Dication dimer 10, formed by coupling (or complexing) of two monomeric radical cations (1$^+$), is attacked by CH$_3$OH to produce 4 or loses two protons to form binaphthyl dimer 11, which upon further oxidation produces 5 or 6.
Intermediate 10 may be formulated as a π-complex, or more likely as a σ-bonded dimer dication which undergoes ring opening as illustrated in Scheme 2-6. Dimer dications are proposed intermediates leading to dehydrodimers (biaryls) frequently observed in the oxidations of aromatic hydrocarbons.\textsuperscript{87,93}

The second order rate law and appearance of products in preparative electrolysis are also consistent with a radical cation disproportionation mechanism (Scheme 2-7). It is the monomeric dication $1^{++}$, formed from disproportionation of two $1^+$, that is attacked by methanol to produce 4. The dication $1^{++}$ at same time can be captured by a neutral 1 in the cage to form dimer dication 10, which produces 11 after losing two protons. 11 upon further oxidation produces 5 or 6, as proposed in Scheme 2-5.
Chapter 2. Anodic Oxidation of Cyclopropynaphthalenes

Scheme 2-6. Ring opening mechanism of dimer dication 10 in CH$_3$CN/CH$_3$OH

Scheme 2-7. Anodic oxidation mechanism of 1 in CH$_3$CN/CH$_3$OH (Disproportionation)
**Oxidation of 1-bromo-4-cyclopropylnaphtalene (2).** Both the LSV and DCV results for 2 are consistent with a rate law for decay of $2^+$ which is second order in radical cation and zero order in methanol. Preparative electrolysis of 2 yields exclusively cyclopropane ring-opened product. These results suggest that the attack of methanol occurs after the rate-limiting step. A mechanism analogous to that proposed for decay of $1^+$ is consistent with these results (Scheme 2-8). Intermediate dication dimer 12 reacts with methanol to produce 7 (and release 2). Because it is not possible to lose “Br” under these conditions, the dimerization pathway ($12 \rightarrow 11$) is effectively “turned off,” and only the monomeric, cyclopropane ring-opened product is produced. The disproportionation is another likely mechanism for the decay of $2^+$, in which the dication $2^{++}$ is attacked by methanol to produce 7.

Scheme 2-8. Anodic oxidation mechanism of 2 in CH$_3$CN/CH$_3$OH
As noted earlier, $2^+$ is longer-lived in CH$_2$Cl$_2$ compared to in CH$_3$CN. This observation is reasonable because CH$_3$CN is more polar than CH$_2$Cl$_2$. In general, oxidation potentials become more positive as the dielectric constant of the solvent decreases, attributable to variations in the solvation energy of the radical cations. The reactivity of radical ions is subject to ion-pairing effects. We suggest that $2^+$ is longer lived in CH$_2$Cl$_2$ because of increased ion pairing (which decreases the rate constant for dimerization).

The rate constant for dimerization of $2^+$, determined by fitting the DCV results to theoretical working curves generated via digital simulation is $3.9 \pm 0.2 \times 10^3$ M$^{-1}$s$^{-1}$ in CH$_2$Cl$_2$. Also, the rate constant for dimerization of $2^+$ ($k_{\text{dim}}$) was determined at various concentrations of CH$_3$CN (in CH$_2$Cl$_2$, Table 2-5). Using these data, it is possible to determine the value of $k_{\text{dim}}$ in CH$_3$CN solvent via extrapolation. A plot of log($k_{\text{dim}}$) vs. log[CH$_3$CN] is linear (Figure 2-47): log($k_{\text{dim}}$) = 4.0786 + 0.2758 log[CH$_3$CN]. Extrapolation to pure CH$_3$CN (19.1M) yields $k_{\text{dim}} = 3.1 \times 10^4$ M$^{-1}$s$^{-1}$. 


Figure 2-47  Variation of \( k_{\text{dim}} \) for \( 2^+ \) with \([\text{CH}_3\text{CN}]\) in CH\(_2\)Cl\(_2\) solvent

\[
y = 0.2758x + 4.0786 \\
R^2 = 0.995
\]

Oxidation of 2-cyclopropynaphthalene (3). The decay of \( 3^+ \) is found to be second order in radical cation and zero order in methanol. A mechanism analogous to that depicted in Scheme 2-5 (involving a dimer dication intermediate 13) is likely operative (Scheme 2-9). The alternative mechanism, disproportionation, is also consistent with second order rate law and product analysis (involving dication 3\(^{++}\)).
2.2.4 Stereoelectronic vs. Thermodynamic Factors

Estimated rate constant for ring opening of 1-cyclopropynaphthalene radical cations. In the presence of methanol, oxidation of cyclopropynaphthalenes 1, 2, and 3 leads mostly to cyclopropane ring-opened products, i.e., the corresponding 1,3-dimethoxypropyl derivatives. However, the radical cation of each of these substrates was found to decay via a rate law second-order in radical cation and zero-order in methanol, which means that methanol attack on the cyclopropane ring must occur after rate-limiting dimerization or disproportionation. Consistent with the observed rate law and nature of the products formed, we suggest that this second-order decay leads to formation of a dimer dication (which can be formulated as either a σ- or π-complex) or dication. The important point is that regardless of the exact nature of the dimer dication or dication, this second-order process must be occurring at a rate significantly faster than methanol-induced cyclopropane ring opening (e.g., $k_{\text{dim}} \left[ 2^+ \right] >> k_{\text{MeOH}} \left[ \text{CH}_3\text{OH} \right]$, Scheme 2-10).
Scheme 2-10. Scheme for estimate of rate constant for CH$_3$OH-induced ring opening of 2$^+$

Utilizing these results, it is possible to use this dimerization process as a “clock” to estimate an upper limit for the rate constant for methanol-induced ring opening of $\alpha$-cyclopropynaphthalene radical cations ($k_{\text{MeOH}}$). In CH$_3$CN solvent, the rate law $k_{\text{dim}}[2^+]^2$ was observed over a range of CH$_3$OH concentrations from 0 to 1.4 M, with $k_{\text{dim}} = 3.1 \times 10^4$ M$^{-1}$s$^{-1}$. The concentration of 2$^+$ never exceeds 0.01 M (the maximum concentration of substrate used in any of these experiments). Assuming that the rate of radical cation dimerization or disproportionation is at least 10 times faster than CH$_3$OH-induced ring opening ($k_{\text{dim}}[2^+] \geq 10 \times k_{\text{MeOH}}[\text{CH}_3\text{OH}]$) one obtains $k_{\text{MeOH}} \leq 20$ M$^{-1}$s$^{-1}$.96
Dinnocenzo reported that the absolute rate constant for the methanol-induced ring opening of \( \text{C}_6\text{H}_5-c-\text{C}_3\text{H}_5^+ \) is \( 9.5 \times 10^7 \) M\(^{-1}\)s\(^{-1}\) in CH\(_3\)CN. Thus, the change from phenyl to 1-naphthyl results in (at least) a six order of magnitude diminution in the rate of cyclopropane ring opening.

**Thermodynamic Considerations.** A possible explanation for the extremely low rate of ring opening of cyclopropynaphthalene radical cations may be related to the relative stability of naphthalene vs. benzene radical cations, i.e., because of the intrinsic stability of the naphthalenes, ring opening is thermodynamically (and thus kinetically) disfavored. Similar arguments have been advanced to explain the extremely low rate of ring opening of several cyclopropane-containing radical anions.

Using the thermodynamic cycle outlined in Scheme 2-11, it is possible to obtain an estimate of \( \Delta G^\circ \) for CH\(_3\)OH-induced ring opening of a cyclopropylarene radical cation in CH\(_3\)CN solvent. The pertinent \( \Delta G^\circ \)'s for reactions (i) \( \rightarrow \) (vi) were obtained as follows:

(i) the oxidation potential of \( \text{Ar}-c-\text{C}_3\text{H}_5 \), (ii) the C-C bond dissociation energy of cyclopropane (BDE\(_{\text{C-C}}\) = 61 kcal/mol) corrected for the radical stabilization energy (RSE) of the different aryl groups,\(^97\) (iii) the bond dissociation energy of a 1\(^o\) R-OCH\(_3\) bond (BDE\(_{\text{C-O}}\) =82 kcal/mol),\(^98\) (iv) the H-O bond strength of methanol (BDE\(_{\text{O-H}}\) = 104 kcal/mol), (v) the standard potential of the H'/H' couple in CH\(_3\)CN (reported by Parker to be -1.88 V vs. NHE),\(^99\) and (vi) the difference in pK\(_a\) between CH\(_3\)CN and the ether oxygen (pK\(_a\)(CH\(_3\)CN) = -10.12; \(^100\) pK\(_a\)(CH\(_3\)CH\(_2\)OCH\(_2\)CH\(_3\)) = -3.59).\(^{101}\)
The oxidation potentials \( E^0 \) of cyclopropylarenes were estimated from ionization potentials of these compounds. Because the cyclic voltammograms for cyclopropybenzene, 1-cyclopropylnaphthalene, and 2-cyclopropylnaphthlene are all irreversible, it is not possible to measure the oxidation potentials of these substrates directly. Using SCF-MO (AM1), ionization potentials (IP’s) were calculated for a series of aromatic hydrocarbons. IP’s calculated via AM1 correlate well to IP’s obtained experimentally via photoelectron spectroscopy\(^{102}\) (Figure 2-48, \( R^2 = 0.995 \)).
Figure 2-48. Comparison of IP’s obtained via AM1 vs. those via experiment

As shown in Table 2-7 and Figure 2-49, a good linear relationship also exists between the IP’s obtained from AM1 and the oxidation potential of the arene ($E^\circ$), $E^\circ(V$ vs. NHE) = 0.9121 × IP - 5.8225. On the basis of this relationship, $E^\circ$ for cyclopropylbenzene, 1-, and 2-cyclopropynaphthalene were estimated to be 2.58, 1.99, and 2.02 V (vs. NHE in CH$_3$CN), respectively. These estimated $E^\circ$'s appear to be quite accurate. For example, the cyclic voltammogram of 9-bromo-10-cyclopropylanthracene is reversible at high sweep rates, with $E^\circ = 0.920$ V (vs. 0.1 M Ag$^+/Ag$),$^{103}$ 1.498 V (vs. NHE). Using the AM1-calculated IP (8.14 eV), $E^\circ$ (estimated) is 1.599 V (vs. NHE).
Table 2-7. Oxidation potentials and AM1-calculated ionization potentials for several aromatic hydrocarbons

<table>
<thead>
<tr>
<th>compound</th>
<th>IP (AM1, eV)</th>
<th>$E^o$ (V vs. NHE) in CH$_3$CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>9.65</td>
<td>3.03</td>
</tr>
<tr>
<td>naphthalene</td>
<td>8.71</td>
<td>2.08</td>
</tr>
<tr>
<td>anthracene</td>
<td>8.12</td>
<td>1.61</td>
</tr>
<tr>
<td>toluene</td>
<td>9.33</td>
<td>2.61</td>
</tr>
<tr>
<td>perylene</td>
<td>7.86</td>
<td>1.3</td>
</tr>
<tr>
<td>chrysene</td>
<td>8.37</td>
<td>1.88</td>
</tr>
</tbody>
</table>

Figure 2-49. $E^o$ as a function of AM1-calculated IP’s

$y = 0.9121x - 5.8255$

$R^2 = 0.9913$
The results of this analysis are summarized in Table 2-8. The surprising fact that emerges is that regardless of the identity of aryl group, all these ring openings are substantially exothermic.

Table 2-8. $\Delta G^0$ for the methanol-induced ring opening of cyclopropylarene radical cations in CH$_3$CN

<table>
<thead>
<tr>
<th>Aryl group</th>
<th>$E^0_{Ar^+/Ar}$ (V vs. NHE)</th>
<th>RSE (kcal/mol)</th>
<th>$\Delta G^0$ (kcal/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenyl</td>
<td>2.58</td>
<td>10.2</td>
<td>-39.1</td>
</tr>
<tr>
<td>1-naphthyl</td>
<td>1.99</td>
<td>13.1</td>
<td>-28.4</td>
</tr>
<tr>
<td>2-naphthyl</td>
<td>2.02</td>
<td>12.5</td>
<td>-28.5</td>
</tr>
</tbody>
</table>

$^a \Delta G^0 = 30.7 - 23.1 E^0_{Ar^+/Ar} - \text{RSE(Ar)} \text{ in kcal/mol.}$

**Stereoelectronic Considerations.** Two conformational extremes are important for cyclopropane rings attached to a $\pi$-system, bisected ($\theta = 0^\circ$) and perpendicular ($\theta = 90^\circ$), where $\theta$ is the angle defined by the cyclopropyl methine C-H bond with respect to the atoms of the adjacent $\pi$-system. In general, the bisected conformation is preferred because overlap between the cyclopropyl HOMO and LUMO of the $\pi$-system is maximal in this conformation.$^{104}$

The conformational preference(s) of 1-cyclopropylnaphthalene radical cation was explored using SCF-MO theory (AM1, C.I.=1). Earlier studies have found that the neutral molecule adopts a conformation midway between bisected and perpendicular ($\theta = 54^\circ$) because the normally preferred bisected is destabilized by steric interactions between the cyclopropyl group and the peri-hydrogens.\textsuperscript{105} In contrast 1-cyclopropylnaphthalene radical cation exhibits no overwhelming conformational preference, presumably because removal of an electron increases the magnitude of the interaction between the cyclopropyl HOMO and the $\pi$-system. Structures with $\theta = 0^\circ$ and $54^\circ$ are degenerate (within 0.1 kcal/mol) and separated by a barrier of approximately 0.5 kcal/mol. For 2-cyclopropylnaphthalene radical cation, AM1 calculations predict the bisected conformation to be favored by 1.4 kcal/mol.

Thus for 1- or 2-cyclopropylnaphthalene radical cations, the bisected conformation is readily accessible, suggesting that stereoelectronic factors are not responsible for the extraordinarily sluggish rate of ring opening.

**Ring opening of cyclopropylarene radical cations.** Dinnocenzo, et al. reported the effect of alkyl substituents on the rate and regiochemistry of the methanol-induced ($S_N2$) ring opening of cyclopropylbenzene radical cations. Generally, alkyl substituents on
the cyclopropane ring increase the rate of ring opening, with nucleophilic attack occurring at the most hindered position (C-2, Scheme 2-12).\textsuperscript{106} These observations were explained on the basis that the alkyl group could stabilize the partial positive charge on the carbon undergoing substitution. It was further argued on the basis of the Hammond’s postulate that these reactions have an early (reactant-like) transition state and that the charge distribution in the transition state was similar to the radical cations themselves.

\[
\text{Ar}^+ \quad \xrightarrow{\text{R}} \quad \text{Ar}^+ \quad \xrightarrow{\text{CH}_3\text{OH}} \quad \text{Ar}^+ \quad \xrightarrow{\text{OCH}_3}\text{H}
\]

Scheme 2-12. Methanol-induced ring opening of cyclopropylarene radical cation

An early (reactant-like) transition state would imply that the rate of the reaction would be only modestly affected by changes in $\Delta G^o$ for the reaction (i.e., $\partial \Delta G^\circ / \partial \Delta G^o < 0.5$). Our results show that for decay of Ar-$c$-C\textsubscript{3}H\textsubscript{5}+, the change from Ar = phenyl to Ar = 1-naphthyl results in at least a six order of magnitude decrease in rate, corresponding roughly to a difference in free energies of activation ($\Delta A\Delta G^\circ$) for these two processes of at least 8.2 kcal/mol. The difference in $\Delta G^o$ for these two processes ($\Delta A\Delta G^o$) is 10.7 kcal/mol. Thus $\Delta A\Delta G^\circ / \Delta A\Delta G^o \geq 0.77$, suggestive of a transition state which is more product- than reactant-like.
As the data in Table 2-8 reveals, two important factors contribute to $\Delta G^0$ for these ring opening reactions: The ability of the aryl group to stabilize the ring-closed radical cation (manifested by the difference in redox potentials, $\Delta E^0_{Ar+/Ar}$) and the ability of the aryl group to stabilize the benzylic radical formed after ring opening ($\Delta RSE$). Of these two, the effect of the aryl group on radical cation stability is far more profound.

These observations are consistent with a transition state for ring opening in which spin density is delocalized over C-1 (the benzylic carbon) and the aromatic ring but charge is highly localized at C-2 and oxygen (e.g., 15). As such, in the transition state, the aryl group can stabilize the radical portion of the developing distonic radical ion (presumably to a lesser degree than for the fully developed radical), but will have little effect on the positive charge (Figure 2-50). (This proposal is consistent with recent transition state calculations for ring opening of C$_6$H$_5$-c-C$_3$H$_5^+$ by CH$_3$OH which reveal that in the progression from reactant to transition state, there is an increase in positive charge at C-2 (from 0.19 to 0.40) at the expense of the phenyl group (0.68 to 0.28).
Figure 2-50. The proposed effect of aryl rings on the stabilities of reactants, transition states and products for CH$_3$OH-assisted cyclopropane ring opening

Thus nucleophile-induced ring opening of cyclopropylnarene radical cations provide an intriguing exception to the Hammond’s postulate in that they are overwhelmingly exothermic, yet in terms of the distribution of charge and spin, have transition states which are more product- than reactant-like. Moreover, the effect of the aromatic ring on the rate is primarily due to changes in the free energy of the reactant, with only a modest effect on the free energy of the transition state for ring opening.

**Implications for the use of cyclopropane-substituted compounds as SET probes.** Cyclopropane-containing substrates are frequently employed as probes for single electron transfer. The implicit assumption in such a study is that if a paramagnetic
intermediate (neutral free radical or radical ion) is produced, it will undergo ring opening. Earlier work dealing with neutral free radicals and ketyl radical anions has shown that the rate constant for ring opening is quite large when the ring-opening is thermodynamically favored. For example, $\Delta G^\circ$ for the cyclopropylcarbinyl $\rightarrow$ homoallyl radical rearrangement (Scheme 1-13) is -3.1 kcal/mol, and the rate constant is $1.2 \times 10^8$ s$^{-1}$. Similarly, ring opening of radical anion 16 (Scheme 2-12) is estimated to be exothermic by about 2 kcal/mol ($R =$ phenyl or vinyl), and the rate constant is $>10^5$ s$^{-1}$.

![Scheme 2-13 Ring opening of cyclopropylphenylketyl radical anion](image)

In the case of Ar-$c$-C$_3$H$_5^+$, despite the fact that ring opening enjoys an enormous thermodynamic driving force, the process occurs at a dramatically slower rate. Clearly, the intrinsic barrier to ring opening is greater for ring opening of these radical cations. The unique activation/driving force relationship for radical cation ring opening is likely attributable to the fact that the process is bimolecular (nucleophile-assisted). The rate of ring opening is governed by the amount of positive charge transmitted to the cyclopropane ring via resonance (Figure 2-53), and the fact that this charge becomes localized in the transition state (e.g., 15).
For neutral radicals or ketyl anions, it is spin rather than charge which is transmitted to the cyclopropyl group upon ring opening. Because ring opening is unimolecular, spin (and charge for the radical anions) is not localized in the transition state and the intrinsic barrier to ring opening is considerably lower.

For cyclopropylarene radical cations, and presumably other systems which would undergo nucleophile-assisted ring opening, the fact that the ring opening reaction may enjoy a potent thermodynamic driving force is no guarantee that the ring opening will occur at an appreciable rate. Indeed, it is likely that many of the substrates discussed herein would fail to detect a bona fide SET process. Thus, these results reveal a new (and unexpected) complication in the design and utilization of SET probes.

2.3 SUMMARY

Radical cations generated from 1-cyclopropynaphthalene (1), 1-bromo-4-cyclopropynaphthalene (2), and 2-cyclopropynaphthalene (3) were studied electrochemically. Oxidation of all these substrates in CH$_3$CN in the presence of CH$_3$OH leads to cyclopropane ring-opened products, i.e., the corresponding 1,3-dimethoxypropynaphthalenes. However, the rate constant for methanol induced ring opening (Ar-c-C$_3$H$_5$\(^+\) + CH$_3$OH $\rightarrow$ ArCH(•)CH$_2$CH$_2$O(H\(^+\))CH$_3$) is extremely small (<20 M\(^{-1}\)s\(^{-1}\) for the 1-cyclopropynaphthalenes) despite the fact that ring opening is exothermic by nearly 30 kcal/mol. These results are explained on the basis of a product-like transition
state for ring opening wherein the positive charge is localized on the cyclopropyl group, and thus unable to benefit from potential stabilization offered by the aromatic ring.
CHAPTER 3. CERIUM (IV) OXIDATION OF CYCLOPROPYLBENZENES AND CYCLOPROPYLNAPHTHALENES

3.1 INTRODUCTION

The kinetics and mechanism of the ring opening of cyclopropylarene radical cations in the presence of nucleophiles have been the subject of numerous investigations. As introduced in Chapter 1, anodic, photochemical and Ce(IV) oxidation of cyclopropylbenzenes all led to cyclopropane ring-opened products. Dinnocenzo, et al. have shown that ring opening of cyclopropylbenzene radical cation occurs via a nucleophile-assisted (i.e., $S_N2$) pathway, which has been well characterized in terms of its stereochemistry, kinetics, regiochemistry and kinetic isotope effects.

In Chapter 2, we have examined the follow-up chemistry of radical cations generated from cyclopropynaphthalenes electrochemically. Although anodic oxidation of all these substrates in the presence of CH$_3$OH led to cyclopropane ring opened products, the rate constant for methanol induced ring opening (if it happens) is extremely small ($< 20$ M$^{-1}$s$^{-1}$) despite the fact that ring opening is exothermic by nearly 30 kcal/mol.

Due to the nature of the electrochemical experiment, radical cations are generated heterogeneously and in high concentration near the electrode. The dimerization or coupling of radical cations are often seen as one of the reaction pathways. The products isolated from our electrolyses of cyclopropynaphthalenes are mainly cyclopropane ring opened monomer and dimer products, and the radical cations of cyclopropynaphthalenes
were found to dimerize or disproportionation before cyclopropane ring opening based on the rate laws from the voltammetric analyses.

In order to confirm the product nature, we performed the homogeneous Ce(IV) oxidation of cyclopropylarenes in CH₃CN/CH₃OH. The cyclopropane-containing substrates chosen for Ce(IV) oxidation are 1-cyclopropylbenzene (1), 1-cyclopropyl-4-methylbenzene (2), 1-cyclopropynaphthalene (3), 1-bromo-4-cyclopropynaphthalene (4), 2-cyclopropynaphthalene (5). In addition, 1-methylbenzene (toluene) and 1-methylnaphthalene were employed for comparison.

![Structures of cyclopropylarenes]

- X = H, 1
- X = CH₃, 2
- X = H, 3
- X = Br, 4
- 5
3.2 RESULTS AND DISCUSSION

3.2.1 Synthesis of Cyclopropylarenes

1-Cyclopropyl-4-methylbenzene (2). Starting with 1-methyl-4-vinylbenzene, 2 was prepared in one step, as shown in Scheme 3-1. The cyclopropyl group was constructed from the vinyl group in the starting compound by reacting with methylene iodide and zinc-copper couple, based on Smith-Simmons’s methods.

Scheme 3-1. Synthesis of 1-cyclopropyl-4-methylbenzene (2)

1-Cyclopropynaphthalene (3), 1-Bromo-4-cyclopropynaphthalene (4) and 2-Cyclopropynaphthalene (5). The construction of cyclopropane ring in 2-position of naphthalene is the same as that in 1-position of naphthalene. Consequently, the methods for synthesis of 3 can be followed for synthesis of 5 by using 2-bromonaphthalene instead of 1-bromonaphthalene as starting material. 4 can be prepared by the bromination of 3. Synthesis of 3 and 4 were shown in Scheme 3-2.
3.2.2 Ce(IV) Oxidation of Cyclopropylbenzenes

**1-Cyclopropylbenzene (1).** Ce(IV) oxidation of 1 in CH$_3$CN mainly produces cyclopropane ring-opened product 1-phenylpropyl-1,3-dinitrate (6, 60.7%), while aromatic nitration products, 1-cyclopropyl-2-nitrobenzene (7, 20%) and 1-cyclopropyl-4-nitrobenzene (8, 7.5%), are also obtained under the condition employed. The ratio of aromatic nitration products are nearly 3:1 (Scheme 3-3).
Chapter 3. Cerium (IV) Oxidation of Cyclopropylbenzenes and Cyclopropynaphthalenes

1-Cyclopropyl-4-methylbenzene (2). Under the exact same condition, Ce(IV) oxidation of 2 also yields cyclopropane ring-opened product 1-(4-methylphenyl)propyl-1,3-dinitrate (9, 67.4%) as major product and aromatic nitration product 1-cyclopropyl-4-methyl-2-nitrobenzene (10, 12.8%) as minor product (Scheme 3-4).

Scheme 3-3. Ce(IV) oxidation of 1-cyclopropylbenzene (1) in CH₃CN

Scheme 3-4. Ce(IV) oxidation of 1-cyclopropyl-4-methylbenzene (2) in CH₃CN
**Toluene.** For toluene, Ce(IV) oxidation under same condition is so slow that 87% starting material is recovered after same period of time of reaction. Only about 1% of side-chain deprotonation product, nitrate 11, is detected by $^1$HNMR (Scheme 3-5).

\[
\text{(NH}_4\text{)}_2\text{Ce(NO}_3\text{)}_6 / \text{CH}_3\text{CN} \\
\text{70 ~ 80°C / 5 min} \\
\]

\[
87\% \text{ (recovered)} \\
1.1\% \\
11 \\
\sim 10\% \\
\]

Scheme 3-5. Ce(IV) oxidation of toluene in CH$_3$CN

3.2.3 Ce(IV) Oxidation of Cyclopropynaphthalenes

**1-Cyclopropynaphthalene (3).** Ce(IV) oxidation of 3 in CH$_3$CN/CH$_3$OH mainly yielded cyclopropane ring-opened 1,3-disubstituted products: 20.4% of 1-(1,3-dimethoxypropyl)naphthalene 12, 35% of 3-methoxy-3-naphthylpropynitrate 13, and 9.1% of 1-naphthylpropyl-1,3-dinitrate 14. In the absence of methanol, Ce(IV) oxidation of 3 in CH$_3$CN gave 47.1% of 14 as major product. It was noted that 3-hydroxy-3-naphthylpropynitrate 15 was formed from 14 during PTLC separation. The reaction is shown in the Scheme 3-6.
Scheme 3-6. Ce(IV) oxidation of 1-cyclopropynaphthalene (3) in CH₃CN/CH₃OH

1-Br-4-cyclopropynaphthalene (4). Like 3, Ce(IV) oxidation of 4 in CH₃CN/CH₃OH yielded mainly cyclopropane ring-opened products, 16, 17 and 18, as shown in Scheme 3-7.
Chapter 3. Cerium (IV) Oxidation of Cyclopropylbenzenes and Cyclopropynaphthalenes

Scheme 3-7. Ce(IV) oxidation of 1-bromo-4-cyclopropynaphthalene (4) in CH$_3$CN/CH$_3$OH

2-Cyclopropynaphthalene (5). Ce(IV) oxidation of 5 in CH$_3$CN/CH$_3$OH yielded similar cyclopropyl ring opened products, 19, 20 and 21, as shown in Scheme 3-8. Alcohol 22 was also noted during PTLC separation.

Scheme 3-8. Ce(IV) oxidation of 1-cyclopropynaphthalene (3) in CH$_3$CN/CH$_3$OH
Chapter 3. Cerium (IV) Oxidation of Cyclopropylbenzenes and Cyclopropynaphthalenes

1-Methylnaphthalene. Ce(IV) oxidation of 1-methylnaphthalene in CH$_3$CN/CH$_3$OH gave mainly side-chain deprotonation products, 23, 24 and 25, as shown in Scheme 3-9. Without methanol, nitrate 23 was the only major product.

![Scheme 3-9. Ce(IV) oxidation of 1-methylnaphthalene in CH$_3$CN/CH$_3$OH](image)

3.2.4 Cyclopropane Ring Opening Mechanism

**Cyclopropylbenzenes.** Like 1, Ce(IV) oxidation of 2 in CH$_3$CN yields mainly cyclopropane ring-opened product and no side-chain deprotonation product is detected. The results suggest that cyclopropane ring opening of $2^+$ is much faster than deprotonation of this radical cation. Obviously, cyclopropane ring strain is the driving
force for the ring opening of cyclopropylbenzene radical cations. The mechanism of oxidation is proposed as in Scheme 3-10.

Scheme 3-10. Ce(IV) oxidation mechanism of 1-methyl-4-cyclopropynaphthalene (2)

**Cyclopropynaphthalenes.** The mechanism of Ce(IV) oxidation of cyclopropynaphthalenes is assumed to be similar to that of cyclopropylbenzenes. The radical cation $3^+$ undergoes nucleophile (e.g., $\text{ONO}_3^-$) assisted ring opening to form benzylic-type radical, which further is oxidized to the corresponding cation and then captured by another molecular of nucleophile to give the final product (Scheme 3-11).
Chapter 3. Cerium (IV) Oxidation of Cyclopropylbenzenes and Cyclopropynaphthalenes

The alternative mechanisms follow ones proposed for anodic oxidation of cyclopropynaphthalenes. Dimerization mechanism: Radical cation $3^+$ dimerizes to form dimer dication, which experiences nucleophile attack to form benzylic-type cation and release neutral $3$. The cation is captured by nuclophile to give 1,3-disubstituted product.

Disproportionation mechanism: Two radical cations of $3$ disproportionate to a neutral $3$ and dication $3^{++}$, which is attacked by methanol to lead the same product. Scheme 3-12 shows the proposed mechanism for decay of $3^{++}$, based on dimerization and disproportionation pathways.
In Chapter 2, we found that although the cyclopropyl group in neutral molecule of 1-cyclopropynaphthalene adopts a conformation midway between bisected and perpendicular \((\theta = 54^\circ)\), the radical cation of this molecule exhibits no overwhelming conformational preference and structures with \(\theta = 0^\circ\) and 54° are degenerate (within 0.1 kcal/mol) and separated by a barrier of approximately 0.5 kcal/mol. Thus for 1-cyclopropynaphthalene radical cations, the bisected conformation is readily accessible, suggesting that stereoelectronic factors are not important in the reactivity of cyclopropynaphthalene radical cations.
3.3 SUMMARY

Ce(IV) oxidation of cyclopropylbenzenes and cyclopropynaphthalenes in the presence of nucleophiles all led to cyclopropane ring opened 1, 3-disubstituted products. For $p$-methylcyclopropylbenzene, the radical cations undergo cyclopropane ring opening rather than deprotonation. Since the bisected conformation is readily accessible for both cyclopropylbenzene and cyclopropynaphthalene radical cations, stereoelectronic factors are not important in reactivity of these radical cations.
4.1 INTRODUCTION

Since radical cations were first proven to be the primary intermediates of the anodic oxidation of anthracene and related compounds by three independent research groups in 1967,\textsuperscript{110,111,112} the follow-up reactions of radical cations of anthracene and derivatives have been the subject of numerous investigations, most of which are attributed to Parker and co-workers.\textsuperscript{113} Radical cations in general are highly reactive species. However, the ease with which radical cations undergo reactions with nucleophiles or form dimeric products can be moderated by suitable structural modification as well as reaction medium conditions. The reaction pathways of radical cations with various nucleophiles have extensively been studied by means of electrochemical techniques.\textsuperscript{114} Detailed studies of reactions of anthracene and substituted anthracene radical cations included hydroxylation,\textsuperscript{115} acetoxylation,\textsuperscript{116} methoxylation\textsuperscript{117} and pyridination.\textsuperscript{118,119}

As shown in Chapters 2 and 3, anodic and Ce(IV) oxidation of cyclopropylbenzenes and cyclopropynaphthalenes all led to cyclopropane ring-opened products. However, while free radical bromination of cyclopropylbenzenes and cyclopropynaphthalenes also gave cyclopropane ring-opened products, the free radical bromination of 9-cyclopropylanthracene and derivatives yielded exclusively hydrogen abstraction products. This variation in the chemoselectivity of bromination of cyclopropylarenes was explained as the result of stereoelectronic factors (Scheme 1-17).
The transition state for the reaction of a cyclopropylarene with a neutral free radical is isoelectronic to that of the reaction of its radical cation with a nucleophile \((\text{Ar-}c\text{-}C_3H_5^+\text{/}X^- \text{ vs. } \text{Ar-}c\text{-}C_3H_5\text{/}X^-)\). Consequently, it is reasonable to suspect that the same stereoelectronic factors may pertain to radical cation chemistry. In this chapter, the chemistry of radical cations generated from 9-cyclopropylanthracene (1) and 9-bromo-10-cyclopropylanthracene (2) is examined electrochemically.

\[ \text{X = } \text{H, 1} \]
\[ \text{X = Br, 2} \]

4.2 RESULTS AND DISCUSSION

4.2.1 Kinetic Analysis from Voltammetry

The mechanism and kinetics of decay of radical cations generated from 1 and 2 were studied electrochemically. All voltammetric measurements were performed in anhydrous CH\textsubscript{3}CN/CH\textsubscript{3}OH with 0.5 M LiClO\textsubscript{4} as supporting electrolyte. A Pt microdisk electrode served as working electrode, and the reference electrode was 0.1 M Ag\textsuperscript{+}/Ag (0.337 V vs. SCE). An ultrasonic system was employed to clean electrode surface between voltammetric runs.
Chapter 4. Anodic Oxidation of Cyclopropynanthracenes

9-Cyclopropynanthracene (1). The cyclic voltammogram of 1 (Figure 4-1) is characterized by an initial oxidation wave ($E_p \approx +780 \text{ mV}$ at 500 mV/sec) and several additional oxidation waves at more positive potentials. In the presence of CH$_3$OH the peaks at more positive potentials are changed but the initial oxidation wave is unaffected (i.e., the peak potential and current remain the same, Figure 4-1).

Figure 4-1. Cyclic voltammogram of 9-cyclopropynanthracene (1) in CH$_3$CN (0.5 M LiClO$_4$, $5 \times 10^{-3}$ M 1, $v = 500 \text{ mV/s}$)
The initial oxidation wave is irreversible at all accessible sweeprates (up to 50 V/sec for our system). Consequently, LSV was an appropriate technique for studying this system. \( E_p \) was found to vary both as a function of sweeprate and substrate concentration, but was independent of the concentration of methanol. Figures 4-2 through 4-4 show typical LSV analyses for \( 1 \), and the results of these experiments are summarized in Table 4-1. These observations are in excellent agreement with a second-order mechanism for radical cation decay (Eq. 4-1).

\[
-d[1^{+*}] / dt = k [1^{+*}]^2
\]  

(4-1)

Figure 4-2. LSV analysis of \( 1 \), \( \partial E_p / \partial \log(v) \). (0.5 M LiClO\(_4\), 2.5 M CH\(_3\)OH, 10 \times 10^{-3} \text{ M } 1, v = 100 \rightarrow 8000 \text{ mV/sec})

\[
y = 20.65x + 692.5 \\
R^2 = 0.9964
\]
Figure 4-3. LSV analysis of \(1\), \(\partial E_P/\partial \log[\text{CH}_3\text{OH}]\). (0.5 M LiClO₄, 0.025→2.5 M CH₃OH, 10 \times 10^{-3} \text{ M } 1, \nu = 400\text{mV/sec})

\[y = 0.1722x + 743.96\]

\[R^2 = 0.0189\]

Figure 4-4. LSV analysis of \(1\), \(\partial E_P/\partial \log[1]\). (0.5 M LiClO₄, 2.5 M CH₃OH, 1.79→20.8 \times 10^{-3} \text{ M } 1, \nu = 100\text{mV/sec})

\[y = -21.356x + 686.94\]

\[R^2 = 0.9983\]
Table 4-1. LSV analysis of the electrochemical oxidation of 1

<table>
<thead>
<tr>
<th>Rate law</th>
<th>$\partial E_p/\partial \log(v)$</th>
<th>$\partial E_p/\partial \log[A]$</th>
<th>$\partial E_p/\partial \log[X]^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k [B]$</td>
<td>29.6$^{b}$</td>
<td>0$^{b}$</td>
<td>0$^{b}$</td>
</tr>
<tr>
<td>$k [B]^2$</td>
<td>19.7$^{b}$</td>
<td>-19.7$^{b}$</td>
<td>0$^{b}$</td>
</tr>
<tr>
<td>$k [B]^2 [X] / [A]$</td>
<td>19.7$^{b}$</td>
<td>0$^{b}$</td>
<td>-19.7$^{b}$</td>
</tr>
<tr>
<td>observed</td>
<td>20.7 ± 0.6</td>
<td>-21.4 ± 0.5</td>
<td>0.17 ± 0.56</td>
</tr>
</tbody>
</table>

$^{a}$X = CH$_3$OH; $^{b}$Theoretical responses

9-Bromo-10-cyclopropylanthracene (2). The cyclic voltammogram of 2 (Figure 4-5) reveals an initial oxidation wave ($E_p \approx +950$ mV at 2000 mV/sec) and subsequent oxidation waves at more positive potentials. However, unlike 1, at higher sweep rates the initial oxidation wave becomes reversible (Figure 4-6).

At higher sweep rates, the DCV reaction order approach is applicable. The results of these experiments are summarized in Figures 4-7→4-8 and Table 4-2.
Figure 4-5. Cyclic Voltammogram of 2 in CH$_3$CN (whole view) (0.5 M LiClO$_4$, 5 $\times$ 10$^{-3}$ M 2, $\nu$ = 2000 mV/sec)

![Cyclic Voltammogram of 2 in CH$_3$CN (whole view)](image1)

Figure 4-6. Cyclic Voltammogram of 2 in CH$_3$CN (partial view) (0.5 M LiClO$_4$, 5 $\times$ 10$^{-3}$ M 2, $\nu$ = 8000 mV/sec)

![Cyclic Voltammogram of 2 in CH$_3$CN (partial view)](image2)
Figure 4-7. DCV analysis of \( 2, \frac{\partial \log(v_c)}{\partial \log[2]} \). (0.5 M LiClO\(_4\), 0.5 M CH\(_3\)OH,
\( 3.7 \rightarrow 13.9 \times 10^{-3} \) M \( 2, \Gamma'_{pc}/\Gamma'_{pa} = 0.5 \))

\[
y = 1.0921x + 5.6297 \\
R^2 = 0.9968
\]

Figure 4-8. DCV analysis of \( 2, \frac{\partial \log(v_c)}{\partial \log[CH_3OH]} \). (0.5 M LiClO\(_4\), 0.25 \rightarrow 5 \) M CH\(_3\)OH, \( 5.0 \times 10^{-3} \) M \( 1, \Gamma'_{pc}/\Gamma'_{pa} = 0.5 \))

\[
y = 1.0829x + 2.8713 \\
R^2 = 0.9922
\]
Table 4-2. DCV analysis of the electrochemical oxidation of 2

<table>
<thead>
<tr>
<th>Rate law</th>
<th>$\partial \log(v_C)/\partial \log[A]$</th>
<th>$\partial \log(v_C)/\partial \log[X]$</th>
<th>$R_{A/B}$</th>
<th>$R_X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k \ [B] \ [X]$</td>
<td>0.0$^b$</td>
<td>1.0$^b$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$k \ [B]^2 \ [X]$</td>
<td>1.0$^b$</td>
<td>1.0$^b$</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>$k \ [A] \ [B] \ [X]$</td>
<td>1.0$^b$</td>
<td>1.0$^b$</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>observed</td>
<td>1.1 ± 0.1</td>
<td>1.1 ± 0.1</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$X = CH$_3$OH; $^b$Theoretical responses.

Two rate laws are consistent with the observed DCV results. (DCV does not allow deconvolution of the individual reaction orders in A and B). However, both CV and LSV permit the separation of the individual reaction orders in A and B. LSV is applicable at lower sweep rates where no reverse (cathodic) wave is observed. At low scan rates, $E_p$ was found to vary as a function of sweep rate and both the concentrations of 2 and CH$_3$OH (Figure 4-9→4-11, and Table 4-3), supporting a rate law that is first-order each in $2^+$, 2, and CH$_3$OH (Eq. 4-2).

$$-d[2^+]/dt = k \ [2^+] \ [2] \ [CH_3OH] \quad (4-2)$$
Figure. 4-9. LSV analysis of 2, \( \partial E_p/\partial \log(v) \). (0.5 M LiClO\(_4\), 0.5 M CH\(_3\)OH, 

\( 5 \times 10^{-3} \) M 1, \( v = 50 \rightarrow 1500 \) mV/sec)

\[ y = 31.774x + 865.24 \]

\[ R^2 = 0.9958 \]

Figure. 4-10. LSV analysis of 2, \( \partial E_p/\partial \log[CH_3OH] \). (0.5 M LiClO\(_4\), 0.5 \rightarrow 5 \) M CH\(_3\)OH, 

\( 5.0 \times 10^{-3} \) M 2, \( v = 50 \) mV/sec)

\[ y = -29.678x + 911.65 \]

\[ R^2 = 0.9988 \]
Figure 4-11. LSV analysis of 2, $\partial E_P/\partial \log([2])$. (0.5 M LiClO$_4$, 1.0 M CH$_3$OH, 2.0→12.4 × 10$^{-3}$ M 2, $v = 200$ mV/sec)

\[ y = -30.275x + 834.31 \]
\[ R^2 = 1 \]

Table 4-3. LSV analysis of the electrochemical oxidation of 2

<table>
<thead>
<tr>
<th>Rate law</th>
<th>$\partial E_P/\partial \log(v)$</th>
<th>$\partial E_P/\partial \log([A])$</th>
<th>$\partial E_P/\partial \log([X])^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k [A] [X]$</td>
<td>$29.6^b$</td>
<td>$0.0^b$</td>
<td>$-29.6^b$</td>
</tr>
<tr>
<td>$k [A] [B]$</td>
<td>$29.6^b$</td>
<td>$-29.6^b$</td>
<td>$0.0^b$</td>
</tr>
<tr>
<td>$k [A] [B] [X]$</td>
<td>$29.6^b$</td>
<td>$-29.6^b$</td>
<td>$-29.6^b$</td>
</tr>
<tr>
<td>observed</td>
<td>$31.8 \pm 0.8$</td>
<td>$-29.7 \pm 0.7$</td>
<td>$-30.3 \pm 0.1$</td>
</tr>
</tbody>
</table>

$^a$X = CH$_3$OH; $^b$Theoretical responses.
At higher sweep rates where the CV becomes partly reversible, differentiation between the rate laws $k[A][B][X]$ vs. $k[B]^2[X]$ can also be achieved by examining the variation of the cathodic to anodic current ratio ($I_{pc}/I_{pa}$) as a function of sweep rate.\cite{89,120}

In Figures 4-12→4-15, the theoretical responses for these two rate laws and the experimental results obtained at several methanol concentration are compared. A substantially better fit to the curve corresponding to the rate law first order each in A and B is observed.\cite{121}

Figure 4-12. Variation of the cathodic to anodic current ratio (-$I_{pc}/I_{pa}$) with sweeprate for the oxidation of 2 (0.0 M CH$_3$OH).
Figure 4-13. Variation of the cathodic to anodic current ratio (-I_{pc}/I_{pa}) with sweeprate for the oxidation of 2 (0.25 M CH₃OH).

Figure 4-14. Variation of the cathodic to anodic current ratio (-I_{pc}/I_{pa}) with sweeprate for the oxidation of 2 (0.5 M CH₃OH).
Figure 4-15. Variation of the cathodic to anodic current ratio (-$I_{pa}/I_{pa}$) with sweep rate for the oxidation of 2 (1.0 M CH$_3$OH).

Electron Stoichiometry (n). The peak current for a CV wave reflects the total number of electrons transferred, including the initial heterogeneous electron transfer, as well as any follow-up hetero- or homogeneous electron transfer. Many examples pertaining to the oxidation of aromatic hydrocarbons show that $n = 1$ for the oxidation wave if the CV is reversible (i.e., the radical cation is stable within the time-frame of the experiment) and that $n = 2$ (or more) if the CV is irreversible (i.e., the follow-up reactions involve the transfer of additional electrons and contribute to the initial oxidation wave). Frequently two or more electrons need to be transferred in order to obtain a stable product.
In addition to constant potential electrolysis or coulometry, CV provides a qualitative means for estimating the n-value for an oxidation wave in accordance with the following equations (Eq. 4-3 and 4-4), which pertain to reversible systems:

\[ |E_p - E_{p/2}| = \frac{56.5}{n} \text{ mV (at 25}^\circ\text{C)} \]  
\[ I_p = (2.69 \times 10^5) n^{3/2} A D_o^{1/2} v^{1/2} C_o^* \]

A plot of \( I_p \) vs. \( v^{1/2} \) is often used to check whether any follow up reactions involve electron transfer and to estimate the number of electrons transferred.

**9-Bromo-10-cyclopropylanthracene (2).** At higher sweeprates, the reversible oxidation wave for 2 corresponds to \( n = 1 \) \((E_{pa} - E_{p/2} = 50 - 60 \text{ mV})\). At lower sweeprates and/or in the presence of methanol, the wave becomes irreversible because follow-up reactions involving 2\(^{+*}\) are occurring. A total of two electrons need to be transferred in order to form 3.

A plot of \( I_p/C_o^* \) vs. \( v^{1/2} \) for the oxidation of 2 (Figure 4-16) suggests that with methanol addition, the slope changes (corresponding to a change from \( n = 1 \) in the absence of methanol to \( n = 2 \) in the presence of methanol).

**9-Cyclopropylanthracene (1).** A plot of \( I_p/C_o^* \) vs. \( v^{1/2} \) for the oxidation of 1 is presented in Figure 4-17. The slope of this line is nearly the same as that observed for 9-bromo-10-cyclopropylanthracene in the presence of methanol. Assuming that the diffusion coefficients of 1 and 2 are similar, this would suggest that the initial oxidation wave for 1 also corresponds to the transfer of two electrons.
Chapter 4. Anodic Oxidation of Cyclopropylanthracenes

Figure 4-16. $I_p/C_o^*$ vs. $v^{1/2}$ plot for 2 at various concentrations of methanol (0.005 M 2, 0.5 M LiClO$_4$ in CH$_3$CN)

Figure 4-17. $I_p/C_o^*$ vs. $v^{1/2}$ plot for 1 in the presence of methanol (0.004 M 1, 0.5 M LiClO$_4$, 2.5 M CH$_3$OH in CH$_3$CN)
4.2.2 Product Analysis from Preparative Electrolysis

**9-Bromo-10-cyclopropylanthracene (2).** The preparative (constant current) electrolysis of 2 was conducted in CH$_2$CN/CH$_3$OH with 0.1 M LiClO$_4$ as the supporting electrolyte. The products isolated from this electrolysis (Scheme 4-1) varied dramatically as a function of the work-up procedure employed. Aqueous work-up (extraction with H$_2$O/ether) yielded exclusively 9-cyclopropyl-9-methoxyanthrone (3). In contrast, non-aqueous work-up (removing solvent by rotary evaporation followed by extraction with CH$_2$Cl$_2$) yielded mainly cyclopropane ring-opened products (4, 5, and 6). The yields of several representative runs are shown in Table 4-4.

![Scheme 4-1. Anodic oxidation of 2 in CH$_3$CN/CH$_3$OH](image-url)
Table 4-4. Yields of products produced in the controlled-current oxidation of 2

<table>
<thead>
<tr>
<th>[CH$_3$OH] (M)</th>
<th>electrons (equiv.)</th>
<th>workup method</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>2.8</td>
<td>aqueous</td>
<td>62$^a$</td>
<td>---$^b$</td>
<td>---$^b$</td>
<td>---$^b$</td>
</tr>
<tr>
<td>2.5</td>
<td>2.7</td>
<td>aqueous</td>
<td>68$^c$</td>
<td>---$^b$</td>
<td>---$^b$</td>
<td>---$^b$</td>
</tr>
<tr>
<td>4.1</td>
<td>2.5</td>
<td>non-aqueous</td>
<td>0.0</td>
<td>7.4$^a$</td>
<td>21.8$^a$</td>
<td>23.2$^a$</td>
</tr>
<tr>
<td>2.5</td>
<td>2.7</td>
<td>non-aqueous</td>
<td>0.0</td>
<td>9.3$^c$</td>
<td>41.0$^c$</td>
<td>12.3$^c$</td>
</tr>
<tr>
<td>0.25</td>
<td>2.5</td>
<td>non-aqueous</td>
<td>0.0</td>
<td>5.8$^c$</td>
<td>12.6$^c$</td>
<td>4.3$^c$</td>
</tr>
</tbody>
</table>

$^a$Isolated yield; $^b$Trace; $^c$Yield determined by $^1$HNMR.

Although substantially different products resulted, the mass balances observed for both the aqueous and non-aqueous work-up procedures were similar (60 - 70 %) leading to the suspicion that the reaction products might be interconverting during non-aqueous workup. Indeed, monitoring of the electrolysis prior to workup by either GC or TLC revealed that only 3 was produced during the electrolysis, suggesting that this compound was the precursor to 4, 5, and 6.

In separate experiments this hypothesis was validated by subjecting 3 to conditions designed to emulate the conditions of the non-aqueous work-up procedure. For example,
treatment of 3 with HBr in CH$_3$CN led to formation of ring-opened bromide 6 in 80 % yield (unoptimized). Similarly, treatment of 3 with HClO$_4$ in CH$_3$CN yielded perchlorate ester 5 in 46 % yield (unoptimized). These results substantiate the contention that cyclopropane ring-opened products 4, 5, and 6 are produced during non-aqueous workup (Scheme 4-2).

![Scheme 4-2. Conversion of product 3 to product 4, 5, or 6 under acidic conditions](image)

9-Cyclopropylanthracene (1). Controlled-current electrolysis of 1 in CH$_3$CN/CH$_3$OH followed by a non-aqueous work-up resulted in the formation of cyclopropane ring-opened products (in analogy to the results observed in the oxidation of 2). However, ring-opened products were also found when an aqueous work-up was employed (Table 4-5). Periodic monitoring of the reaction mixture during the electrolysis by TLC and GC revealed that 9-cyclopropyl-10-methoxyanthracene (7) was formed early in the electrolysis, but was converted to other products upon further electrolysis (The yield of 7 reached a maximum of 37 % after two equivalents of electrons were transferred). A small quantity of anthraquinone (8) was detected, even at the early stages.
of the electrolysis. Bianthrone (9) was also detected in runs at low methanol concentration.

![Chemical structures](image)

Table 4-5. Yields of products produced in the controlled-current oxidation of 1

<table>
<thead>
<tr>
<th><a href="M">CH$_3$OH</a></th>
<th>Electrons (equiv.)</th>
<th>workup method</th>
<th>yield, %$^a$</th>
<th>7</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>8</th>
<th>9</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>2.0</td>
<td>aqueous</td>
<td>37.0</td>
<td>19.8</td>
<td>1.2</td>
<td>0.0</td>
<td>13.9</td>
<td>---$^b$</td>
<td>20.4</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>3.0</td>
<td>aqueous</td>
<td>3.6</td>
<td>27.6</td>
<td>32.0</td>
<td>0.0</td>
<td>3.6</td>
<td>---$^b$</td>
<td>17.8</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>3.0</td>
<td>non-aqueous</td>
<td>0.0</td>
<td>2.8</td>
<td>41.4</td>
<td>20.4</td>
<td>13.0</td>
<td>---$^b$</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>2.5</td>
<td>non-aqueous</td>
<td>0.0</td>
<td>---$^b$</td>
<td>12.8</td>
<td>16.7</td>
<td>---$^b$</td>
<td>8.0</td>
<td>---$^b$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Yield determined by GC or $^1$HNMR; $^b$Trace.

**Characterization of Perchlorate Ester 5.** Surprisingly, perchlorate ester 5 was successfully isolated and characterized despite the unstable and extremely explosive nature
Chapter 4. Anodic Oxidation of Cyclopropylanthracenes

of alkyl perchlorates. Recent studies have demonstrated that perchlorate ion can manifest nucleophilic properties in the presence of extraneous nucleophiles (e.g., halide ions).\textsuperscript{122} Because of the novelty of this compound, some discussion of its characterization is warranted. The IR spectrum of 5 exhibited two peaks at 1230 and 1260 cm\textsuperscript{-1} (Cl-O asymmetric stretching) and a peak at 1040 cm\textsuperscript{-1} (Cl-O symmetric stretching), which are a characteristic of covalent organic perchlorates. The \textsuperscript{1}HNMR spectrum of 5 possesses a triplet shifted unusually downfield (\(\delta = 4.8\) ppm vs. TMS) corresponding to the CH\(_2\) \(\alpha\) to the perchlorate group. Finally, the molecular weight (and formula) were confirmed using FAB-MS, HRMS, and elemental analysis.

4.2.3 Reaction Mechanism

**Oxidation of 9-Cyclopropylanthracene (1).** LSV results for 1 show that decay of 1\(^+\) in CH\(_3\)CN/CH\(_3\)OH is second-order in radical cation and zero order in CH\(_3\)OH. Consequently, CH\(_3\)OH attack must occur after the rate-limiting step. Based on these results, a disproportionation mechanism for decay of the radical cation from 1 is proposed (Scheme 4-3).\textsuperscript{123} Because the dication will invariably be more reactive toward nucleophiles than the radical cation, it is reasonable to suppose that \(k_2[\text{CH}_3\text{OH}] > k_1[1]\) so that the overall rate law reduces to \(k_1[1^+]^2\). A nearly identical mechanism for decay of 9-alkylanthracene radical cations in CH\(_3\)CN/H\(_2\)O, studied by stopped-flow kinetics was recently reported by Fujita and Fukuzumi.\textsuperscript{124} This mechanism is further supported by the bulk electrolysis results which reveal that 7 is the product initially produced during the oxidation. The isolation of 7 and 3 as the only detectable products provides direct
evidence that the cyclopropyl group survives both the radical cation and dication stages of oxidation.

Further oxidation of 7\(^{125}\) forms 7\(^{++}\) which likely undergoes oxidative methyl transfer (Scheme 4-4), as proposed in Parker’s studies of the anodic oxidation of dimethoxydurene,\(^ {126}\) to form 11. Further oxidation yields 10 which leads to the isolated product 3 after nucleophilic attack of methanol.

Scheme 4-3. Anodic oxidation mechanism of 1 (from 1 to 7)
Because the anodic process produces $\text{H}^+$, some of 3 is converted to cyclopropane ring-opened products either during the electrolysis or upon work-up.

**Oxidation of 9-Bromo-10-cyclopropylanthracene (2).** CV, DCV and LSV results for 2 are all consistent with a rate law for decay of $2^+$ which is first order each in radical cation, parent compound and methanol ($-\text{d}[2^+)/\text{d}t = k[2^+][2][\text{CH}_3\text{OH}]$). The reason why $2^+$ does not decay via a disproportionation mechanism (as proposed for $1^+$) may be due to the fact that the bromine substituent deactivates the aromatic ring making the removal of a second electron from $2^+$ energetically prohibitive. (Parker found that $E^\circ$ for 9-bromoanthracene was more positive than anthracene by 90 mV). As a
consequence of having the disproportionation pathway effectively “turned-off,” decay of
the radical cation follows a different pathway, presumably involving nucleophilic attack of
CH₃OH prior to or during the rate-limiting step. However, the appearance of 2 in the rate
law was somewhat unexpected.

A mechanism which accounts for the presence of 2 in the rate law involves
formation of π-complex between 2 and 2⁺ (12, Scheme 4-5). Radical cation/neutral
molecule complexes involving aromatic radical cations have been characterized
spectroscopically, and are usually formulated as a π-dimer with the two molecules
oriented face to face, with charge and spin delocalized into both rings.⁸⁷

Methanol attack on the dimer radical cation 12 in the rate determining step to form
the radical catoin of a methoxy derivative, which quickly loses a HBr to produce 7⁺. The
follow-up reaction of 7⁺ is the same as proposed in Scheme 4-4, producing the final
product 3. The total electrons from 2 to 3 is two, which is consistent with the results from
CV analysis.
Ring Opening of 3 Under Acidic Conditions. As discussed earlier, cyclopropane ring-opened products (4, 5, and 6) are not the primary oxidation products of the oxidation of 1 or 2. Indeed, these ring-opened products are produced from 3 by reaction with ClO$_4^-$, Br$^-$, or CH$_3$OH, facilitated by the H$^+$ produced during the electrolysis. Presumably, ring opening could occur via an S$_N$1 or S$_N$2' pathway (Scheme 4-6). The S$_N$1 pathway is unlikely, however, because we have already shown that cation 10 (an intermediate in the electrochemical oxidation) does not lead to ring-opened products.
(presumably because of stereoelectronic considerations). In contrast, because of the sp$^3$ canter in 3, the cyclopropyl group is essentially freely rotating and can readily achieve the conformational requirements for ring opening by the $S_{N2}'$ mechanism (i.e., alignment of the C-O bond with the p-component of the vicinal C$_1$-C$_2$ or C$_1$-C$_3$ bonds).

![Diagram](image)

Scheme 4-6. Proposed ring opening mechanism of 3 under acidic condition

4.2.4 Stereoelectronic vs. Thermodynamic Factors

**Semiempirical MO Calculations.** In order to assess the role of conformation on the reaction pathway for the anodic oxidation of cyclopropylanthracenes, semiempirical MO calculations were performed on 1, 1$^+$, and other potential intermediates generated during the oxidation of 1. Towards this end, the AM1 approximation developed by
Chapter 4. Anodic Oxidation of Cyclopropylanthracenes

Dewar et al and implemented through MOPAC 6.0 was employed. The keyword "C.I.=1" was used for $1^+$ (i.e., the half-electron approximation). For comparison, analogous calculations were performed on cyclopropylbenzene, as well as its corresponding radical cation and dication. The results are summarized in Table 4-6.

Table 4-6. AM1-calculated $\Delta H^o$ for conformational interconversion (perpendicular → bisected) for the 9-cyclopropylanthracene and cyclopropylbenzene system

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H^o$, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.2</td>
</tr>
<tr>
<td>$1^+$</td>
<td>4.5</td>
</tr>
<tr>
<td>$1^{2+}$</td>
<td>0.7</td>
</tr>
<tr>
<td>10</td>
<td>3.5</td>
</tr>
<tr>
<td>$C_6H_5-c-C_3H_5$</td>
<td>-0.3</td>
</tr>
<tr>
<td>$C_6H_5-c-C_3H_5^{+}$</td>
<td>-4.6</td>
</tr>
<tr>
<td>$C_6H_5-c-C_3H_5^{2+}$</td>
<td>----- *</td>
</tr>
</tbody>
</table>

*Although the geometry and energy of the perpendicular conformation were successfully obtained, geometry optimizations of the bisected conformation always led to a cyclopropane ring-opened structure.
For cyclopropylbenzene, the bisected conformation is found to be more stable by 0.3 kcal/mol, in reasonable agreement with the experimental value of 1.4 kcal/mol reported by Closs and Klinger. The bias in favor of the bisected conformation is predicted to increase for the radical cation, although there are no experimental values available for comparison.

As was reported earlier for the neutral molecule, the perpendicular conformation is predicted to be more stable than the bisected for 1, 1+, 1²⁺ because of unfavorable steric interactions (i.e., interaction of the cyclopropyl group with the peri-hydrogens).

These calculations also suggest that 1, 1+, 1²⁺, or 10 cannot achieve a true bisected conformation. For the “bisected” conformation of each of these species, the anthryl system adopts a “butterfly” geometry, and the cyclopropyl methine C-H bond is out-of-plane by as much as 20° (Figure 4-18).

Figure 4-18. AM1-predicted geometry for the “bisected” and perpendicular conformations of 1⁺

pseudo-bisected conformation
Steroelectronic Consideration. AM1 calculations (Table 4-6) suggest that 9-cyclopropylanthracene exists primarily in the perpendicular conformation, and that the same also holds true for the other intermediates likely generated in the oxidation of 1 ($1^+$, $1^{2+}$, or 10). In 1969, Bauld et al. reported the ambient temperature EPR spectrum of $1^+$ (generated from treatment of 1 with H$_2$SO$_4$). The observed hyperfine coupling constant to the cyclopropyl methine hydrogen ($a_{\text{H}\beta}$) was reported to be 4.0 G. This coupling is the result of hyperconjugation, and the magnitude of $a_{\text{H}\beta}$ depends upon both the angle ($\theta$) between the C-H bond and the $\pi$-orbital containing the unpaired electron, and the spin density at ($\rho$) in this orbital: $a_{\text{H}\beta} = [A + B \cos^2(\theta)]\rho$, where A and B are constants. ($a_{\text{H}\beta}$ is expected to be near zero for the bisected conformation since the C-H bond is orthogonal to the $\pi$-system). Assuming that $\rho$ and B were approximately equal for both $1^+$ and 9-methylanthracene$^\cdot$ (yielding $\theta_{\text{avg}} = 60^\circ$), the spectrum was interpreted on the basis of a freely rotating cyclopropyl group with a slight preference for the bisected conformation.
As noted above, however, AM1 calculations suggest the perpendicular conformation is lower in energy and that because of steric constraints, the bisected conformation is not truly bisected (i.e., the anthracene ring adopts a butterfly geometry with $\theta \approx 70 - 75^\circ$ rather than $90^\circ$, Figure 4-18). Utilizing AM1, the calculated $a_H^\beta$'s for the pseudo-bisected and perpendicular conformations of $1^+$ are 0.68 G and 7.0 G, respectively. The experimentally observed value of 4.0 G falls slightly toward the upper end of this range, suggesting a) the pseudo-bisected and perpendicular conformations are both important, with the latter slightly favored, or b) that the ground state conformation of $1^+$ is midway between these two conformations.

However, the important point is that the experimentally observed $a_H^\beta$ appears to be too large to be attributed to $1^+$ existing preferentially in the bisected conformation (or even the pseudo-bisected conformation). Whether the perpendicular conformation actually predominates as the calculations suggest (Table 4-6), or whether the conformation is intermediate between the pseudo-bisected and perpendicular conformations (as the combined EPR and computational results suggest), either via time-averaged equilibration or as a discrete conformation, is not resolved.

Dinnocenzo has provided convincing evidence that ring opening of cyclopropylarene radical cations is nucleophile-assisted (e.g., $S_N2$). However, the stereoelectronic requirements for ring opening may only be met when the cyclopropylarene is in the bisected conformation (Scheme 4-7).
Thus, if the bisected conformation is not accessible to $1^+$, the failure of the cyclopropane ring in this system to undergo ring opening may be attributed to unfavorable stereoelectronic factors. Consequently, the initial oxidation products arise primarily from nucleophilic attack on the aromatic ring (Scheme 4-7).

**Thermodynamic Consideration.** In its reaction with methanol, cyclopropylbenzene radical cation yields the thermodynamically-favored (ring-opened product). Although 9-cyclopropylanthracene radical cation is intrinsically more stable than Ph-c, because of resonance, the same resonance stabilization is also available to both the ring-opened benzylic-type radical (formed after CH$_3$OH-induced ring opening) and to the cyclohexadienyl-type radical formed from addition of CH$_3$OH to the aromatic
There is no obvious reason to expect a reversal in the stabilities of these two products. Consider the stability of the following two pairs of radicals ($\Delta H^\circ$'s were obtained using SCF-MO, AM1 approximation, Scheme 4-8)).

![Scheme 4-8. Stability of benzylic-type radical and cyclohexadienyl-type radical](image)

Although the difference is smaller in the anthracene system, the cyclopropane ring-opened benzyl-type radical is predicted to be substantially more stable than the cyclopropane ring-closed cyclohexadienyl-type radical for both the anthryl and phenyl systems. This prediction is reasonable in light of the relative stabilities of benzyl vs. cyclohexadienyl radicals, and the effect of cyclopropane ring strain.

Using the thermodynamic cycle, as introduced in Chapter 2 (Scheme 2-11), $\Delta G^\circ$ for methanol-induced ring opening of $1^+$ in CH$_3$CN is estimated (Table 4-7). It was found that although $\Delta G^\circ$ is smaller in anthracene system, all these ring opening are substantially exothermic.
Table 4-7. $\Delta G^0$ for the methanol-induced ring opening of cyclopropylarene radical cations in CH$_3$CN

<table>
<thead>
<tr>
<th>Aryl group</th>
<th>$E_{\text{Ar}+/\text{Ar}}^0$ (V vs NHE)</th>
<th>RSE (kcal/mol)</th>
<th>$\Delta G^0$ (kcal/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenyl</td>
<td>2.58</td>
<td>10.2</td>
<td>-39.1</td>
</tr>
<tr>
<td>1-naphthyl</td>
<td>1.99</td>
<td>13.1</td>
<td>-28.4</td>
</tr>
<tr>
<td>9-anthyl</td>
<td>1.48</td>
<td>16.4</td>
<td>-21.1</td>
</tr>
</tbody>
</table>

$^a\Delta G^0 = 30.7-23.1 E_{\text{Ar}+/\text{Ar}}^0 - \text{RSE(Ar)}$ in kcal/mol.

Thus, for both the phenyl and anthryl systems, ring opening is expected to be the thermodynamically preferred pathway. The fact that the thermodynamically least stable product is formed from cyclopropylanthracene radical cations suggests that its chemistry may be under kinetic, rather than thermodynamic control.

**The Story Has Not Ended, Design of A New “Probe”.** Although the stereoelectronic argument above is reasonable, there is no direct experimental evidence that conformation of cyclopropylarene radical cations does affect their reactivity (i.e., cyclopropane ring opening). Moreover, the energy difference between bisected and perpendicular conformation becomes smaller and smaller from 1 to 1$^+$ to 1$^{++}$, although perpendicular conformation of these species are still the lowest energy conformation. For 1-cyclopropynaphthalene radical cation (see Chapter 2), the bisected conformation is found to be readily accessible and stereoelectronic factors was suggested being not
Chapter 4. Anodic Oxidation of Cyclopropylanthracenes

responsible for the extremely sluggish rate of ring opening. Consequently, based on thermodynamic consideration, a transition state which is more product-like than reactant-like was proposed for methanol-induced cyclopropane ring opening of 1-cyclopropylnaphthalene radical cation (see Chapter 2). The similar considerations also pertain to 9-cyclopropylanthracene radical cation and much higher intrinsic barrier to nucleophile-induced ring opening is expected (Figure 4-19).

Figure 4-19. The proposed effect of aryl rings on the stabilities of reactants, transition states and products for CH$_3$OH-assisted cyclopropane ring opening

Thus, using the picture described in Figure 4-19, the fact that 1$^+$ does not undergo ring opening can be explained on a kinetic basis. Due to much higher intrinsic barrier to nucleophile-induced cyclopropane ring opening of 1$^+$, cyclopropyl group survives
oxidation, and alternatively, other process such as aromatic ring oxidation (e.g.,
nucleophilic attack) occurs (also see Chapter 5).

However, stereoelectronic factors can not be excluded from above consideration
(Figure 4-19). Stereoelectronic factors may make a contribution to the intrinsic barrier
(i.e., the barrier may be greater than predicted in Figure 4-19). Thus, a new “probe” needs
to be designed to answer the question: Are streoelectronic factors important in ring
opening reactions of cyclopropylarene radical cations?

It is our hypothesis that if the cyclopropane ring does not open during oxidation of
an anthracene substrate in which the cyclopropyl group is locked in the bisected
conformation, stereoelectronic factors can be discounted, and the failure of these species
for ring opening can be wholly attributed to a product-like transition state when the
positive charge is highly localized (in analogy to cyclopropynaphthalenes). In the light of
this consideration, a new “probe”, 1-spiroaceanthracene and derivatives (13, 14, 15), will
be synthesized to test this hypothesis.
4.3 SUMMARY

Reactions of radical cations generated from 9-cyclopropylanthracene (1) and 9-bromo-10-cyclopropylanthracene (2) in the presence of methanol have been investigated electrochemically. The major products arising from oxidation of both substrates are attributable to CH$_3$OH attack at the aromatic ring (occurring at the radical cation stage for 2 and the dication stage for 1) rather than CH$_3$OH-induced cyclopropane ring opening. The cyclopropyl group in these anthryl systems adopts a perpendicular conformation which may not meet the stereoelectronic requirements for cyclopropane ring opening at either the radical cation or dication stage. However, an alternative interpretation for the survival of cyclopropyl group during oxidation of 1 and 2 based on thermodynamic and kinetic consideration also contributes to the barrier for ring opening. A transition state which is more product-like than reactant-like is proposed and it demonstrates that aromatic ring oxidation occurs due to higher intrinsic barrier to nucleophile-induced cyclopropane ring opening.
CHAPTER 5. CERIUM (IV) OXIDATION OF CYCLOPROPYLANTHRACENES 
AND 9,10-DIMETHYLANTHRACENE

5.1 INTRODUCTION

5.1.1 Initiation of The Project

In Chapter 4, we observed that anodic oxidation of 9-cyclopropylanthracene and 
9-bromo-10-cyclopropylanthracene led to aromatic ring oxidation products. Unlike 
cyclopropylbenzene, the cyclopropyl group in these two anthryl substrates survived the 
oxidation processes. The higher barrier to ring opening of these radical cations is 
attributable to stereoelectronic factors and/or to the fact that positive charge is highly 
localized in the transition state for ring opening, and is thus unable to be stabilized by the 
anthryl system. A detailed analysis of these two considerations was presented in Chapters 
2 and 4. Because the cyclopropane ring in the anthryl system does not open during the 
oxidation process, it is difficult to separate the relative importance of these two factors on 
the methanol-induced ring opening of cyclopropylanthracene radical cations.

The ring opening of cyclopropylarene radical cation is similar to the deprotonation 
of corresponding alkylarene radical cation (Eq. 5-1 and Eq. 5-2).

\[
\text{Ar}^\circ\text{c-C}_3\text{H}_5 + \text{B} \rightarrow \text{Ar-CH}_2(\bullet)\text{CH}_2\text{CH}_2\text{B}^+ \quad (5\text{-}1)
\]

\[
\text{Ar}^\circ\text{-CH}_3 + \text{B} \rightarrow \text{Ar-CH}_2(\bullet) + \text{BH}^+ \quad (5\text{-}2)
\]

It was expected that an intramolecular competition experiment might confirm or rule out 
the role of stereoelectronic factors in the cyclopropane ring opening reaction. The
substrates designed for this experiment are \( p \)-methylcyclopropylarenes. In Chapter 3, we reported that Ce(IV) oxidation of 1-cyclopropyl-4-methylbenzene produced solely ring-opened products (no side-chain deprotonation products were observed. If the deprotonation products were obtained from oxidation of 9-cyclopropyl-10-methylandanthracene under same condition, it would have given us a clue about existence of stereoelectronic factors. Because cyclopropyl group in 9-cyclopropyl-10-methylandanthracene adopts a perpendicular conformation while in 1-cyclopropyl-4-methylbenzene it prefers to adopt a bisected conformation, the product ratio (or nature) of cyclopropane ring opening vs. side-chain deprotonation may reflect the role of stereoelectronic effects on these reactions.

Tolbert’s work\(^{68,69}\) on Fe(III) oxidation of 9,10-dimethylandanthracene (DMA) gave us the basis to test our hypothesis. Indeed, we obtained deprotonation products (e.g. 9-cyclopropyl-10-methoxymethyleneanthracene) from Ce(IV) oxidation of 9-cyclopropyl-10-methylandanthracene at room temperature in CH\(_3\)CN/CH\(_3\)OH. However, when reaction temperature was lowered to 0°C, ring oxidation products were produced exclusively. This surprising result suggests that the radical cation of 9-cyclopropyl-10-methylandanthracene undergoes neither cyclopropane ring opening nor deprotonation. Instead, nucleophilic addition to the aromatic ring is probably the initial reaction of anthryl system.

Consequently, the attempt to evaluate stereoelectronic factors by using competition experiments (ring opening vs. deprotonation) was destined to fail because the assumption on which these experiments were based (9-methylandanthracene radical cations deprotonate) is likely invalid. This result brought into question a number literature results which claimed that alkylanthracene radical cations quickly deprotonate. Thus, experiments were
designed to ascertain whether or not alkylanthracene radical cations do undergo deprotonation. The substrates chosen for this study are 9-cyclopropylanthracene (1), 9-bromo-10-cyclopropylanthracene (2), 9-cyclopropyl-10-methylenanthracene (3) and 9,10-dimethylenanthracene (4).

5.1.2 Literature Review

The cyclopropane ring opening and alkyl deprotonation of radical cations generated from benzene derivatives has been reviewed in detail in Chapter 1. The following highlights literature pertaining to the oxidation of alkylanthracenes. There are basically three groups who have done most of significant work on this area.

**Parker’s Group.** The reactions of the radical cations of anthracene and its 9-mono- and 9,10-disubstitued methyl, phenyl, methoxy and halogen derivatives have been studied by Parker using electrochemical methods. These studies mainly revealed products derived from nucleophilic addition of solvent (water, acetic acid or alcohol) to the radical cations, except for 10-methoxy-9-methylenanthracene. Proton loss from methyl-substituted anthracene radical cations was not observed. Anodic
acetoxylation$^{132,134}$ and methoxylation$^{132}$ of anthracene, 9-methylnanthracene and 9,10-dimethylnanthracene (DMA, 4) produce 9,10-disubstituted derivatives (Scheme 5-1).

![Scheme 5-1. Anodic oxidation of anthracene and substituted anthracenes](image)

Lead tetraacetate oxidation of anthracene in benzene$^{135}$ was reported to give 9,10-diacetate-9,10-dihydroanthracene, but lead tetraacetate oxidation of DMA was reported to yield side-chain substituted diacetate (Scheme 5-2)$^{136}$. The mechanism for this reaction was suggested to involve the initial formation of 9,10-diacetate-9,10-dimethylnanthracene A, followed by elimination of acetic acid to give B, and rearrangement of B to give C as an intermediate (Scheme 5-2)$^{137}$. Heating A in acetic acid resulted in the formation of C in quantitative yield$^{132}$ which supported this mechanism.
Tolbert’s Group. Tolbert and coworkers studied chemical and biomimetic oxidation of 9,10-dialkylanthracenes in CH$_3$CN/H$_2$O in 1990’s (see Chapter 1.2). They found that when a methyl group is present, rapid deprotonation of these radical cations occurs. For example, meso-methylanthracenes were oxidized by one-electron oxidant (e.g., Fe(III)) to hydroxymethyl derivatives (Scheme 5-3). No significant ring oxidation products were observed. On the other hand, they observed that when an ethyl group is present, stereoelectronic effects inhibit deprotonation of the radical cation. Meso-ethylanthracenes was found to undergo a facile chemical or biochemical oxidative elimination of ethylene to yield an anthrone rather than deprotonation product (Scheme 5-3).
Chapter 5. Cerium (IV) Oxidation of Cyclopropylanthracenes and 9,10-Dimethylantracene

More recently, iodine\textsuperscript{138,139}, Ce(IV)\textsuperscript{140} and biochemical oxidation\textsuperscript{71} of 9-mono-, and 9,10-disubstituted-anthracenes were reported. Oxidation of 9-alkylanthracenes by I\textsubscript{2} in CHCl\textsubscript{3}/pyridine led to nuclear oxidation product. In contrast, oxidation of 9-alkyl-10-methylanthracenes gave side-chain oxidation products (Scheme 5-4).
Chapter 5. Cerium (IV) Oxidation of Cyclopropylanthracenes and 9,10-Dimethylantracene

Scheme 5-4. Iodine oxidation of 9-alkyl-, and 9-alkyl-10-methyl-anthracenes

For aceanthracene and 9-methylaceanthracene, oxidation under same conditions led to predominantly side-chain oxidation products (Scheme 5-5).

Scheme 5-5. Iodine oxidation of aceanthracene and 9-methylaceanthracene

Ce(IV) oxidation of 9-alkylantracene and 9,10-dialkylantracene in CH$_3$CN/H$_2$O was also reported. When R was methyl, ethyl and cyclopropyl, nuclear oxidation products were obtained. The rate of loss of alkyl or hydrogen was H > CH$_3$ > C$_2$H$_5$. However,
oxidation of aceanthracene mainly produced side-chain oxidation product. The product
distribution of these reactions is shown in Scheme 5-6, in which the number below each
product is the area percent obtained from GC (not yields).

![Scheme 5-6. Ce(IV) oxidation of alkylanthracenes in CH$_3$CN/H$_2$O](image)

The results obtained from Tolbert’s group obviously conflict with those from
Parker’s group in terms of initial oxidation products. Thus, the decay mechanism of
alkylanthracene radical cations, namely side-chain vs. nuclear oxidation, is unclear.

**Camaioni’s Group.** Cu(II)-catalyzed peroxydisulfate oxidation of anthracene and
alkylanthracenes in CH$_3$CN in the presence of water or acetic acid was extensively studied
by Camaioni and coworkers.$^{141,142,143}$ For 9-methylnanthracene,$^{72,73}$ side-chain and nuclear
oxidation products and the dimeric compound, lepidopterene, were produced. The product nature is depended on solvent system being used. In CH$_3$CN/H$_2$O, the ring oxidation products, 9-hydroxy-9-methylanthrone and its dehydronation product 9-methyleneanthracene, are predominant, while in CH$_3$CN/HOAc, the side-chain oxidation products like 9-anthracenylmethyl acetate is mainly produced (Scheme 5-7).

Scheme 5-7. Cu$^{2+}$-S$_2$O$_8^{2-}$ oxidation of 9-methylanthracene

Similar oxidations were also performed for the other related substrates such as 9-phenylethylanthracene and DMA, and the products are similar to those obtained from oxidation of 9-methylanthracene (Scheme 5-8).
A mechanism was proposed where the initially formed radical cation underwent competing proton loss and reversible nucleophile addition reactions. The preferred reaction pathway was observed to be structure and medium dependent. It was also noted that acidity of medium might play a role in the product nature of the oxidation. However, the detailed mechanism for the formation of side-chain oxidation product was still unsolved.

**Other Groups.** Sugiyama\textsuperscript{144} in 1987 reported direct alkoxylation of anthracene with some lower alcohols and ethylene glycol monoalkyl ethers, or monoacetate in the presence of cerium(IV)tetrakis(trifluoro acetate), and the expected alkoxylated anthracene derivatives were obtained (Scheme 5-9). Fujita and Fukuzumi\textsuperscript{145} in 1993 found that
Fe(III) oxidation of 9-benzylanthracene in CH$_3$CN led to nuclear oxidation product, 9-benzyl-9-hydroxyanthrone (Scheme 5-9). The decay kinetics of 9-benzylanthracene radical cation in CH$_3$CN was studied by using a stopped flow spectrophotometer. In 1991, Oyama, M., et al.\textsuperscript{146} studied substituent effects on the reaction kinetics of electrogenerated 9-substituted 10-phenylanthracene radical cation with water and methanol. While the products of the reactions of 9,10-diphenylanthracene radical cation with methanol were 9,10-dialkoxy-9,10-diphenylanthracene,\textsuperscript{147} the isolated product was 9-methoxy-9-phenylanthrone in all reaction of other 9-substituted-10-phenylanthracene radical cation with methanol (Scheme 5-9). In the reactions with water, the product was hydroxy form instead of the methoxy one. The reaction kinetics and mechanism of these radical cations were studied in detail by pulse-electrolysis stopped-flow method.

![Scheme 5-9. Oxidation of anthracenes and substituted anthracenes](image-url)
5.2 RESULTS AND DISCUSSION

5.2.1 9-Cyclopropylanthracene and 9-Bromo-10-cyclopropylanthracene

In Chapter 4, the follow-up chemistry of radical cations generated from 9-cyclopropylanthracene (1) and 9-bromo-10-cyclopropylanthracene (2) in the presence of methanol were examined electrochemically. It is found that these radical cations do not undergo unimolecular or methanol-induced cyclopropane ring opening and products isolated are attributable to methanol addition to aromatic ring. In an extension of this work, we began an examination of ceric (IV) ammonium nitrate (CAN) oxidation of 1 and 2 in CH₃CN/CH₃OH, based on the fact that Ce(IV) is a typical one-electron oxidant.

**9-Cyclopropylanthracene (1). Ce(IV) Oxidation of 1 in 9:1 (v/v)**

CH₃CN/CH₃OH at room temperature mainly produces 9-cyclopropyl-10-methoxyanthracene (5) and 9-cyclopropyl-9-methoxyanthrone (6). Some anthraquinone (7) and 9,10-dimethoxy derivative (8) were also formed (Scheme 5-10). The results are summarized in Table 5-1. The nature of the reaction products is consistent with the literature and is also consistent with the results from our electrochemical oxidation (see Chapter 4).
Scheme 5-10. Ce(IV) oxidation of 1 in CH$_3$CN/H$_2$O

Table 5-1. Product yields of Ce(IV) oxidation of 1 in CH$_3$CN/CH$_3$OH

<table>
<thead>
<tr>
<th>Substrate (mmol)</th>
<th>Mole Ratio (Ce(IV)/1)</th>
<th>Product Yields (%)$^a$</th>
<th>1</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.225</td>
<td>2</td>
<td></td>
<td>10</td>
<td>29</td>
<td>17</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>0.122</td>
<td>4</td>
<td></td>
<td>0</td>
<td>22</td>
<td>48</td>
<td>21</td>
<td>2</td>
</tr>
</tbody>
</table>

$^a$ Isolated yields.

Since Ce(IV) is known to be a one-electron oxidant, the mole ratio of two reactants (Ce(IV)/substrate) reflects the number of electrons transferred in an oxidation.
reaction. Table 5-2 showed the effect of mole ratio of 1 to Ce(IV) on product yield distribution. Obviously, 5 is a two-electron oxidation product, which is initially produced and than further oxidized to a four-electron product 6.

Table 5-2. Product distribution of Ce(IV) oxidation of 1 in different mole ratios of Ce(IV):1

<table>
<thead>
<tr>
<th>Substrate (mmol)</th>
<th>Mole Ratio (Ce(IV)/1)</th>
<th>Product Yields (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0.025</td>
<td>1</td>
<td>61</td>
</tr>
<tr>
<td>0.025</td>
<td>2</td>
<td>29</td>
</tr>
<tr>
<td>0.025</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>0.025</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> GC/HPLC yields, only 1, 5, 6 were analyzed.

9-Bromo-10-cyclopropylanthracene (2). For 2 under similar condition, only 6 is produced as major product (Scheme 5-11). Some anthraquinone (7) is also formed during oxidation, which is attributable to trace water present in the solvent. The results are shown in table 5-3.
Chapter 5. Cerium (IV) Oxidation of Cyclopropylanthracenes and 9,10-Dimethylantracene

![Scheme 5-11. Ce(IV) oxidation of 2 in CH$_3$CN/CH$_3$OH](image)

Table 5-3. Product yields of Ce(IV) oxidation of 2 in CH$_3$CN/CH$_3$OH

<table>
<thead>
<tr>
<th>Substrate (mmol)</th>
<th>Mole Ratio (Ce(IV)/2)</th>
<th>Product Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.143</td>
<td>2.1</td>
<td>60$^a$</td>
</tr>
<tr>
<td>0.021</td>
<td>2.1</td>
<td>76$^b$</td>
</tr>
</tbody>
</table>

$^a$ Isolated yields; $^b$ HPLC yields.

For the oxidation of 2, two moles of electrons are needed to form product 6. It is noted that 5 was not formed during oxidation of 2 and HBr was produced in the solution. The product nature and yields are similar to those observed in our electrochemical studies (see Chapter 4).
Oxidation Mechanism of 1 and 2. The oxidation mechanism for 1 and 2 is proposed in Scheme 5-12. Radical cation 1+ can be either attacked by CH$_3$OH followed by oxidation or disproportionated to a dication followed by CH$_3$OH attack to form methoxy substituted cation. Our electrochemical results and results from Fujita and Fukuzumi’s Fe(III) oxidation of 9-benzylanthracene revealed that the 9-substituted anthracene radical cation undergoes disproportionation$^{145}$ to give the corresponding dication, which is caught by methanol to form the methoxy substituted cation followed by rapid proton loss to produce 5. From 1 to 5, two electrons must be transferred. Radical cation 5+ demethylates to a ketyl radical which experiences further oxidation to the corresponding cation, followed by methanol attack to form 6. From 5 to 6, two more electron transfers must be transferred. For 2, it is radical cation or dimer radical cation (complex) that is attacked by methanol based on our electrochemical results. Since HBr was produced and no 5 was detected, the mechanism is better proposed as in Scheme 5-12. However, loss of HBr was questioned by Oyama, et al.$^{146}$ From 2 to 6, a two electron transfer is needed. The final product 6 is similar to those obtained from oxidation of 9-phenylanthracene and 9-bromo-10-phenylanthracene.$^{146}$
Unlike cyclopropylbenzenes, radical cations generated from 1 and 2 do not experience methanol-induced ring opening but rather methanol attack to aromatic ring. The possible reasons for the lack of reactivity of the cyclopropyl group were discussed earlier. However, regardless of the interpretation, the survival of cyclopropyl group in 1 and 2 during oxidation processes makes a case that the assumption (that cyclopropane ring opened products will be obtained if the radical cation is an important reaction
intermediate) being used is misleading, and suggest that caution should be exercised in the use of cyclopropane-containing systems as radical cation probes.

5.2.2 9-Cyclopropyl-10-methylnanthracene and 9,10-Dimethylnanthracene

9-Cyclopropyl-10-methylnanthracene (3). Results for the Ce(IV) oxidation of 3 in CH₃CN/CH₃OH under two conditions are summarized in Scheme 5-13 and Table 5-4. The two-electron oxidation products 9 and 10 were obtained. At 0 °C, only the nuclear oxidation product, 9-cyclopropyl-10-methyl-9,10-dimethoxyanthracene (10), was produced in a 90.5% yield. When reaction temperature is increased to 45 °C, side-chain oxidation product, 9-cyclopropyl-10-methoxymethylnanthracene (9), along with 10 was also obtained. The cyclopropyl group survived during the oxidation processes and behaved just like any other alkyl substituent. The reaction proceeded quantitatively and mass balance is greater than 95%. The product yields were determined by ¹H NMR with (CH₃)₃SiOSi(CH₃)₃ as an internal standard.

![Scheme 5-13. Ce(IV) oxidation of 3 in CH₃CN/CH₃OH](image-url)
Table 5-4. Product yields of Ce(IV) oxidation of 3 in two reaction conditions

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction Conditions</th>
<th>Product Yields (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>1</td>
<td>0 °C / 30 min</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>45 °C / 30 min</td>
<td>37.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> <sup>1</sup>HNMR yields.

**9,10-Dimethylanthracene (4).** Results for the Ce(IV) oxidation of 4 under CH<sub>3</sub>CN/CH<sub>3</sub>OH in different conditions are summarized in Scheme 5-14 and Table 5-5. The two-electron oxidation products, 9,10-dimethoxy-9,10-dimethylanthracene (12) and 9-methoxymethyl-10-methylanthracene (11) were obtained. As found for the oxidation of 3, at 0 °C, nuclear oxidation product 12 is sole product detected, while at 45 °C both nuclear and side-chain oxidation products 11 and 12 were formed. The product yields and mass balance are very good. To answer the question as to whether or not product 11 is derived from 12, a control experiment (run 3 in Table 5-5) was performed in the following manner: Oxidation of 4 in CH<sub>3</sub>CN/CH<sub>3</sub>OH was run at 0 °C for 30 min, then the reaction solution was divided into two portions. Portion one was directly worked up and analyzed by <sup>1</sup>HNMR. Portion two was heated to 45 °C for another 30 min and then worked up and analyzed. The product nature and yields were the same as those in two other independent experiments (run 1 and run 2). From these results, it is obvious that the side-chain oxidation product 11 comes from nuclear oxidation product 12 at higher temperature.
Chapter 5. Cerium (IV) Oxidation of Cyclopropylanthracenes and 9,10-Dimethylanthracene

\[
\text{4} \xrightarrow{1.9 \text{ eq. (NH}_4\text{)}_2\text{Ce(NO}_3\text{)}_6, \text{CH}_3\text{CN / CH}_3\text{OH (9:1)}} \text{11} + \text{12}
\]

Scheme 5-14. Ce(IV) oxidation of 4 in CH₃CN/CH₃OH

Table 5-5. Product yields of Ce(IV) oxidation of 4 in different conditions

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction Conditions</th>
<th>Product Yields (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 °C / 30 min</td>
<td>0.0 98.3</td>
</tr>
<tr>
<td>2</td>
<td>45 °C / 30 min</td>
<td>40.8 53.0</td>
</tr>
<tr>
<td>3</td>
<td>portion 1 0 °C / 30 min, then portion 2 45 °C /30 min</td>
<td>0.0 43.0 94.3 49.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> <sup>1</sup>H NMR yields.

Ce(IV) oxidation of 4 in CH₃CN in the absence of methanol at 0 °C gave side-chain oxidation product 14, which was thought to be converted from intermediate compound 13 during workup (Scheme 5-15). Since 13 is extremely unstable, its isolation is difficult. On the other hand, conversion from 13 to 14 is expected to be much easier,
even at lower temperature. One experiment was designed to confirm that side-chain oxidation product is not initial oxidation product in the following manner: The oxidation was conducted in the CD$_3$CN at 0 °C and the reaction mixture was directly analyzed by $^1$HNMR before workup and after workup. Figure 5-1 shows the $^1$HNMR of starting material 4 (a), and the reaction mixture before workup (b) and after workup (c).

Obviously, after reaction and before workup (b), almost all of 4 is consumed and no signal attributable to side-chain oxidation product 14 was detected (no $\delta = 6.5$ singlet in $^1$HNMR, which corresponds to methylene protons attached to nitrate group). This experiment revealed that initial oxidation product(s) was anthryl ring oxidation product (13, which is unstable and easy to be converted) rather than side-chain oxidation product (14).

![Scheme 5-15. Ce(IV) oxidation of 4 in CH$_3$CN](image)

Scheme 5-15. Ce(IV) oxidation of 4 in CH$_3$CN
Figure 5-1. $^1$HNMR of 4 (a), reaction mixtures before workup (b) and after workup (c)
**Control Experiment.** In order to confirm that the observed side-chain oxidation products are formed from nuclear oxidation products, the following control experiments were run (Scheme 5-16). Compound 10 was heated in CDCl$_3$ at 50°C for one hour and no reaction occurred. However, when two drops of H$_3$PO$_4$ were added, the product 9 was produced. It was noted that protons present in the solution catalyze the conversion of 10 to 9. Because under conditions of Ce(IV) oxidation protons were produced from CH$_3$OH (formation of one mole of oxidation product 10 can introduce two moles of protons), side-chain oxidation products are formed from nuclear oxidation products.

![Chemical structure and reactions]

Scheme 5-16. Control experiment to test whether 10 can be converted into “deprotonation” product 9 under conditions of Ce(IV) oxidation.
5.2.3 Nuclear vs. Side-Chain Oxidation

Our results from Ce(IV) oxidation of 3 and 4 in CH$_3$CN/CH$_3$OH reveal that the initial oxidation products are nuclear oxidation products rather than side-chain oxidation products. The latter are formed from the former under acidic conditions at higher temperatures. There are two questions will be discussed in this section: Why do the radical cations of alkylanthracene undergo nucleophilic addition rather than deprotonation? Where do the side-chain products come from and how are they formed?

**Oxidation Mechanism of 4.** The mechanism for the Ce(IV)-induced oxidation of 4 is shown in Scheme 5-17, and is similar to those proposed for 9,10-dialkylanthracenes. One electron oxidation of 4 by Ce(IV) generates 4$^+$. CH$_3$OH attack on 4$^+$ forms 9-methoxy-9,10-dimethylanthracene radical, which upon removal of another electron by Ce(IV) produces the corresponding cation. The cation is captured by a molecule of methanol to form the addition product 10.

![Scheme 5-17. Oxidation mechanism of 4 in CH$_3$CN/CH$_3$OH](image)
**Decay Pathway of Alkylarene Radical Cations.** The fact that radical cations generated from alkylbenzenes (e.g., toluene and polymethylbenzenes) undergo “fast deprotonation” has been accepted as a typical reaction pathway of alkyl aromatic compounds (Chapter 1). The pKₐ of toluene radical cation is negative (-13 in CH₃CN, -20 in DMSO), which seems to be consistent with this conclusion because deprotonation of toluene radical cation is exothermic (suppose that CH₃OH is the base in the reaction, the pKₐ of its conjugated acid is -2 → -4). However, this rationale is questioned based on the fact that alkylanthracene radical cations do not undergo deprotonation even if deprotonation of these anthryl radical cations is also exothermic although less so than for toluene radical cations (the pKₐ of 9-methylanthracene radical cation is also around -6.4). This situation is analogous to the methanol-induced cyclopropane ring opening of cyclopropylanthracene radical cation which is disfavored due to a higher intrinsic barrier because of the localized positive charge in the transition state. Instead, nucleophilic addition of methanol to alkylanthracene radical cations become predominant. Since the mechanism of deprotonation of an alkylarene radical cation is similar to that of ring opening of a cyclopropylarene radical cation, we suggest that an analogous transition state picture can be applied for deprotonation process of alkylarene radical cations (Figure 5-2).

In Figure 5-2, a product-like transition state for deprotonation was proposed, in which spin density is delocalized over the benzylic carbon and the aromatic ring, but charge is highly localized at methyl-hydrogen and methanol-oxygen. As such, in the transition state, the aryl group can stabilize the radical portion of the radical ion, but will
have little effect on the positive charge. The effect of the aromatic ring on the rate of deprotonation is primarily due to changes in the free energy of the reactant, with only a modest effect on the free energy of the transition state for deprotonation.

Figure 5-2. Proposed effect of different aryl groups on the stabilities of reactants, transition states, and products for deprotonation of ArCH$_3^+$

Thus, for alkylanthracene radical cations, due to higher intrinsic energy barrier, deprotonation process is basically “turn off” and nucleophilc addition to aromatic ring becomes kinetically favored.

Sehested and Holcman$^{150}$ studied reactions of the radical cations of methylated benzene derivatives in aqueous solution and measured the rate constants for proton loss reaction and nucleophilic addition reaction of these radical cations. They found that nucleophilic addition is faster than proton loss but is highly reversible (Scheme 5-18). The
deprotonation product is the isolated product since proton loss of radical cation is irreversible.

\[
\begin{align*}
\text{CH}_3+ & \quad \text{CH}_2-\text{H}_2\text{O} \\
\text{HO}^+ & \quad \text{H}_2\text{O}^+ -\text{H}_2\text{O} \\
\end{align*}
\]

Scheme 5-18. Nucleophilic addition vs. deprotonation of toluene radical cation

For alkylbenzene radical cations, Scheme 5-18 describing two competing decay pathways can be pictured in the reaction energy diagram shown in Figure 5-3. Nucleophilic addition to toluene radical cation is the kinetically favored process and deprotonation of this radical cation is thermodynamically favored process. Since the intrinsic energy barrier is lower for deprotonation process of toluene radical cation (compared to 9-methylantracene radical cation, see Figure 5-2), the deprotonation is the observed pathway under certain conditions (e.g., relatively long reaction time or higher temperature).
It was also noted by Sehested and Holcman\textsuperscript{150} that the rate constants for deprotonation of methylated benzene radical cations decreases by three orders of magnitude as the number of methyl groups increases from one to five. This means that more stable radical cation is less likely to deprotonate because the intrinsic barrier for deprotonation is higher and thus it is kinetically disfavored (Figure 5-2).

For alkylanthracene radical cation, as shown in Figure 5-2, the intrinsic barrier is so high for deprotonation process that no deprotonation product is produced (Figure 5-4). Instead, nucleophilic addition predominates.
Figure 5-4. Proposed reaction energy diagram for 9-methylandthracene radical cation

Conversion Mechanism of Product 10 to 9. A likely mechanism for the conversion of 10 to 9 is shown in Scheme 5-19.
The methoxy group in 10 is protonated under acidic conditions, and methanol is eliminated at higher temperature. The resulting 9-methoxy-9-methyl-10-methyleneanthracene (15) is then converted into 9. This mechanism is further conformed by isolating 15 as an intermediate product.

Elimination of a molecule of nucleophile (e.g., H$_2$O or CH$_3$CO$_2$H) from addition products to form 9-methyleneanthracene derivatives under acidic conditions was also reported by Camaioni$^{143}$ in his studies (e.g., Scheme 5-8). A similar mechanism for product interconversion was proposed by Camaioni$^{143}$ for solvolysis of 9,10-diethyl-9,10-dihydroxyanthracene catalyzed by perchloric acid in CH$_3$CN/H$_2$O (Scheme 5-20). The “deprotonation” product is formed from the addition product under acidic condition.
Scheme 5-20. Mechanism of solvolysis of 9,10-diethyl-9,10-dihydroxanthracene in
 \( \text{H}^+ / \text{H}_2\text{O} \)

**Stereoelectronic vs. Thermodynamic Factors.** Stereoelectronic effects on deprotonation of alkylanthracene radical cations have been reported by Tolbert, et al.\textsuperscript{69} If the alkylanthracene radical cation does not undergo deprotonation, stereoelectronic factors can not be evaluated. Stereoelectronic factors if any may increase the intrinsic barrier to deprotonation as shown in Figure 5-1.

A very good question arose here: Does the radical cation of 9-cyclopropyl-10-methylnanthracene (3) deprotonate at higher temperature? If it does this result might argue for the existence of stereoelectronic factors. In chapter 3, it was found that the radical cation of 1-cyclopropyl-4-methylbenzene undergoes cyclopropane ring opening rather than deprotonation. However, the cyclopropyl group in 3 survives a similar oxidation
process. The reversal of product nature might reflect the stereoelectronic effects on
cyclopropane ring opening of these radical cations. On the other hand, if it does not then
the intrinsic barrier for deprotonation as well as cyclopropane ring opening are both high
and stereoelectronic factors (if any) can not be evaluated. The possible decay pathways of
\(3^+\) was shown in Scheme 5-21.

![Scheme 5-21](image)

Scheme 5-21. Possible decay pathways of 9-cyclopropyl-10-methylanthracene radical
cation

**A Note on Reaction Conditions and Product Identification.** The reaction
conditions for Ce(IV) oxidation of alkylanthracenes are very important in evaluating
product nature and distribution. The reaction produces protons from either solvent or
added nucleophiles (e.g., H\(_2\)O, CH\(_3\)OH or CH\(_3\)CO\(_2\)H). These protons present in the
solution can catalyze the interconversion of the products and proper temperature will
realize or speed up this process. It is dangerous to propose a mechanism only based on
the nature of the products isolated without considering the effects of reaction conditions
(e.g., temperature) on product distribution. Put more succinctly, these results suggest that
in several literature studies, products attributed to the deprotonation of a radical cation
may have been formed by a different pathway.

It was also found in our Ce(IV) oxidation of 9,10-dialkylantracenes that the
parent ions of nuclear oxidation products (e.g., 10, 12) were hard to detect by mass
spectrometry, and the side-chain products (e.g., 9, 11) do not go through the GC (they
decompose or interconvert in our GC temperature). As a result, 1H NMR was employed
to analyze our products.

These experimental notes can partially explain the conflicting results reported from
the literature. For example, the product yields and distribution have been analyzed by GC
or GC-MS in some groups. Also, it is difficult to compare the product nature and
distribution in a set of reactions when the reaction conditions (e.g., temperature) are
different.

5.3 SUMMARY

Ce(IV) oxidation of 9-cyclopropylanthracenes and 9,10-dimethylanthracene in
CH3CN/CH3OH all led to aromatic nuclear oxidation products. The radical cations
generated from these substrates undergo neither cyclopropane ring opening nor
deprotonation but nucleophilic addition. Side-chain oxidation products from Ce(IV)
oxidation of methylated anthracenes were formed from nuclear oxidation products under acidic and higher temperature conditions. A reaction energy diagram describing the reactions of arene radical cations was proposed based on thermodynamic consideration. The results demonstrate that side-chain oxidation products formed from the oxidation of alkylanthracenes cannot be attributed solely (if at all) to the deprotonation of radical cations.
The studies presented in the previous chapters detail the rich chemistry of cyclopropylarene radical cations. Anodic and Ce(IV) oxidation of both cyclopropylbenzenes and cyclopropynaphthalenes (e.g., 1-cyclopropylbenzene, 1-cyclopropyl-4-methylbenzene, 1-cyclopropynaphthalene, 1-bromo-4-cyclopropynaphthalene and 2-cyclopropynaphthalene) in CH$_3$CN/CH$_3$OH leads to cyclopropane ring-opened products (i.e., corresponding 1,3-dimethoxypropylarenes). Utilizing cyclic, derivative cyclic and linear sweep voltammetry, it was found that decay of radical cations generated from cyclopropynaphthalenes (e.g., 1-cyclopropynaphthalene, 1-bromo-4-cyclopropynaphthalene, and 2-cyclopropynaphthalene) in CH$_3$CN/CH$_3$OH is second order in radical cation and zero order in methanol. The radical cations generated from these naphthyl substrates are shown to disproportionate or dimerize before undergoing ring opening.

Dinnocenzo, et al. have reported that ring opening of 1-cyclopropylbenzene radical cation occurs via a nucleophile-induced (i.e., $S_N^2$) pathway and the absolute rate constant for the methanol-induced ring opening is $9.5 \times 10^7$ s$^{-1}$M$^{-1}$. The rate constant estimated for methanol-induced ring opening (Ar-$c$-C$_3$H$_5^+$ + CH$_3$OH → ArCH(•)CH$_2$CH$_2$O(H$^+$)CH$_3$) of cyclopropynaphthalene radical cations is extremely small (<20 s$^{-1}$ M$^{-1}$ for 1-cyclopropynaphthalenes). Thus, the change from phenyl to 1-naphthyl results in (at least) a six order of magnitude diminution in the rate of cyclopropane ring opening despite the
fact that ring opening for both aryl systems is exothermic (by nearly 40 kcal/mol for phenyl and 30 kcal/mol for 1-naphthyl).

AM1 calculations have shown that 1-cyclopropynaphthalene radical cation exhibits no overwhelming conformational preference (earlier studies have found that the neutral molecule adopts a conformation midway between bisected and perpendicular). Thus for both 1- or 2-cyclopropynaphthalene radical cations, the bisected conformation is readily accessible, suggesting that stereoelectronic factors are not responsible for the extraordinarily sluggish rate of ring opening.

Based on these results, a product-like transition state for ring opening of cyclopropylarene radical cations was proposed, in which spin density is delocalized over C-1 (the benzylic carbon) and the aromatic ring, but charge is highly localized at C-2 and oxygen. As such, in the transition state, the aryl group can only stabilize the radical portion of the developing distonic radical ion (presumably to a lesser degree than for the fully developed radical), but will have little effect on the positive charge (Figure 6-1). Consequently, the effect of the aromatic ring on the rate is primarily due to changes in the free energy of the reactant, with only a modest effect on the free energy of the transition state for ring opening.
Figure 6-1. The proposed effects of aryl rings on the stabilities of reactants, transition states and products for methanol-induced cyclopropane ring opening

While cyclopropylbenzene radical cations undergo rapid methanol-induced ring opening and cyclopropynaphthalene radical cations disproportionate or dimerize before undergoing slow ring opening, the radical cations generated from 9-cyclopropylanthracenes were found not to undergo cyclopropane ring opening at all. The major products arising from both electrochemical and Ce(IV) oxidation of 9-cyclopropylanthracene and 9-bromo-10-cyclopropylanthracene in CH$_3$CN/CH$_3$CN are attributable to CH$_3$OH attack at the aromatic ring rather than CH$_3$OH-induced
cyclopropane ring opening (e.g., 9-cyclopropyl-9-methoxyanthrone was produced). An analogous (more product-like) transition state picture (Scheme 6-1) can be applied for cyclopropane ring opening of these anthryl radical cations, based on similar thermodynamic and kinetic consideration. Because of higher intrinsic barrier to nucleophile-induced cyclopropane ring opening of these anthryl radical cations, nucleophilic addition occurs predominantly. The stereoelectronic effects may be another additional factor to this intrinsic barrier because the cyclopropyl group in these anthryl systems adopts a perpendicular conformation which may not meet the stereoelectronic requirements for cyclopropane ring opening at either the radical cation or dication stage.

To our surprise, Ce(IV) oxidation of 9-cyclopropyl-10-methylanthracene and 9,10-dimethylanthracene in CH$_3$CN/CH$_3$OH also leads to nuclear (aromatic ring) oxidation products. The radical cations generated from these anthryl substrates were shown to undergo neither cyclopropane ring opening nor side-chain deprotonation but nucleophilic addition to aromatic ring (e.g., Scheme 6-1). Side-chain oxidation products from Ce(IV) oxidation of these methylated anthracenes were found to be converted from nuclear oxidation products under acidic and higher temperature conditions.
Scheme 6-1. Decay pathways of 9-cyclopropyl-10-methylantracene radical cation in CH$_3$CN/CH$_3$OH

Because the mechanism of side-chain deprotonation of an alkylarene radical cation is similar to that of ring opening of a cyclopropylarene radical cation (Scheme 6-1), a similar transition state picture is also proposed for deprotonation reactions of alkylarene radical cations. Thus, for alkylantracene radical cations, due to higher intrinsic energy barrier, deprotonation process is basically “turned off” and nucleophilic addition to aromatic ring becomes kinetically favored.

Cyclopropane-containing substrates are frequently employed as probes for single electron transfer. The implicit assumption in such a study is that if a paramagnetic intermediate (neutral free radical or radical ion) is produced, it will undergo ring opening. Earlier work dealing with neutral free radicals and ketyl radical anions has shown that the
rate constant for ring opening is quite large when the ring-opening is thermodynamically favored.

In the case of cyclopropylarene radical cations, despite the fact that ring opening enjoys an enormous thermodynamic driving force, the process occurs at a dramatically slower rate (for naphthyl system) or not at all (for anthryl system). Clearly, the intrinsic barrier to ring opening is greater for ring opening of these radical cations. The unique activation/driving force relationship for radical cation ring opening is likely attributable to the fact that the process is bimolecular (nucleophile-assisted). The rate of ring opening is governed by the amount of positive charge transmitted to the cyclopropane ring via resonance, and the fact that this charge becomes localized in the transition state (Figure 6-1). For neutral radicals or ketyl anions, it is spin rather than charge which is transmitted to the cyclopropyl group upon ring opening. Because ring opening is unimolecular, spin (and charge for the radical anions) is not localized in the transition state and the intrinsic barrier to ring opening is considerably lower. For cyclopropylarene radical cations, and presumably other systems which would undergo nucleophile-assisted ring opening, the fact that the ring opening reaction may enjoy a potent thermodynamic driving force is no guarantee that the ring opening will occur at an appreciable rate. Indeed, it is likely that many of the substrates discussed herein would fail to detect a bona fide SET process. Thus, these results reveal a new (and unexpected) complication in the design and utilization of SET probes.
CHAPTER 7. EXPERIMENTAL

7.1 GENERAL

7.1.1 Instrumentation Description

Melting points were determined on a Thomas Hoover capillary melting point apparatus and were uncorrected. Nuclear magnetic resonance spectra (\(^1\)H, \(^{13}\)C, 2D) were obtained on either a 270 MHz Bruker or a 400 MHz Varian FT NMR spectrometer. All chemical shifts are reported in \(\delta\) units relative to TMS (\(\delta 0.00\) ppm) for qualitative analysis and \((\text{CH}_3)_3\text{SiOSi(CH}_3)_3\) (\(\delta 0.00\) ppm) for quantitative analysis in CDCl\(_3\). Infrared spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer with Omnic software package. IR band were reported with \(\nu\) in units of cm\(^{-1}\). Ultraviolet spectra were obtained on a Hewlett Packard HP 8452A diode array spectrophotometer and reported with \(\lambda\) in units of nm and \(\varepsilon\) in units of M\(^{-1}\)cm\(^{-1}\). Low resolution mass spectra data were obtained from a Fisons VG Quattro triple quadrupole mass spectrometer. Electron impact ionization, chemical ionization and fast atom brombordant were employed for MS analysis. GC/MS was performed on Fisons 8060 GC with VG Quattro MS or on a Hewlett Packard model 5890 gas chromatograph with an HP methylsilicone capillary column interfaced with an HP 5097B EI mass spectrometer and an HP series computer. Gas chromatographic analyses were routinely performed on a Hewlett Parkard HP 5890A instrument equipped with FID detector, and an HP 3393A reporting integrator. Analyses were accomplished on an Alltech Econo-CAP SE-54 capillary column (30 \(\times\) 0.25mm).
Analytical and preparative HPLC separations were accomplished on a Beckman instrument using a Microsorb C-18 reverse phase column (anal. 5µm, 4.6mm ID × 25cm; prep. 5µm, 21.4mm ID × 25cm) with acetonitrile/water solvent mixtures. Flash chromatography (Merck, grade 9385 silica gel, 230 - 400 mesh, 60Å) and thin layer chromatography (anal.: Whatman, silica gel plates, 250 µm layer, UV\textsubscript{254}; prep.: Analtech, Silica Gel G & GF Preparative UNIPLATES, 20 × 20 cm, 500 microns) were performed using the solvent systems specified in the specific experiments.

7.1.2 Electrochemical Experiments

Electrochemical measurements were performed on an EG & G Princeton Applied Research (EG & G / PAR) model 273 potentiostat/galvanostat interfaced to an MS-DOS computer. The detailed instrumentation employed for cyclic and linear sweep voltammetry has been described early.\textsuperscript{79,152}

\textbf{Voltammetry.} Voltammetric measurements were performed on solutions which contained 0.5 M LiClO\textsubscript{4} in CH\textsubscript{3}CN (in the presence or absence of methanol, as required). The solutions were prepared by weighing 0.532 g LiClO\textsubscript{4} (or other electrolyte) into an oven-dried 10 mL volumetric flask then placing the volumetric flask, together with all voltammetry cell pieces, in a Baxter DP-22 vacuum drying oven under vacuum (30-40 mmHg) at 40 °C for at least 8 hours. Purified and dried CH\textsubscript{3}CN or/and CH\textsubscript{3}OH were added to the septum-sealed volumetric flask with an oven and vacuum-dried syringe(s). The resulting solution was transferred to the argon-purged voltammetry cell. The electroactive substance was added and the solution continued to be purged with argon.
A three-electrode voltammetry cell was utilized. The Pt microdisk working electrode (0.32 mm in diameter) was prepared for use by polishing with alumina slurry as outlined in the BAS electrode polishing kit (part NO. MF-2056). The Ag/Ag\(^{+}\) (0.10 M in CH\(_3\)CN, 0.337 V vs. SCE) reference electrode was made as described early\(^{152}\). A Pt wire (2 cm in length, 2 mm in diameter) was used as auxiliary electrode. The voltammetry cell was placed in a Fisher FS-14 solid state/ultrasonic tank filled with water. Between voltammetry runs the ultrasonic system was activated for 30 seconds to clean the working electrode surface. Positive-feedback iR compensation was set by monitoring the current response. The iR compensation was increased until oscillation and then backed off to 90% of that value. The reading error of peak potential from a cyclic voltammogram is within 1-2 mV. All experiments were performed at ambient temperature (23 °C).

**Bulk Electrolysis.** Preparative electrolysis was performed on solutions which contained 0.1 M LiClO\(_4\) in CH\(_3\)CN containing CH\(_3\)OH. The blank solutions were prepared similarly as in voltammetry. A conventional H-cell, with two compartments separated by a medium glass frit (22 mm in diameter), was utilized. 60 mL of the electrolyte solution was partitioned equally between the two compartments of an oven then vacuum-dried, fully assembled H-cell under argon. The electro-active substrate was added to the anodic compartment, and both anodic and cathodic compartments were purged for at least 10 minutes with argon before electrolysis.

The working electrode was built from a Pt gauze (45 mesh, 30 mm \(\times\) 20 mm). A 0.5 mm diameter by 4 cm piece of Pt wire was soldered to a 0.5 mm diameter piece of Ag wire. The Pt wire was sealed in an OD Pyrex tube and leaving the Pt partly outside and
the Ag inside the tube. The Pt mesh was then spot welded the Pt wire. The Pt gauze was shaped to conform to the electrolysis cell. The auxiliary electrode was made with copper wire (2 mm in diameter). The one end of copper wire was fabricated in shape of cycles with a diameter of 2 cm. A Ag/Ag⁺ (0.10 M in CH₃CN) electrode was used for reference.

All electrolysis experiments were performed at ambient temperature (23 °C). Constant current electrolysis were performed at a current range from -25 to -40 mA. Both anodic and cathodic compartments purged with Argon, and set in ultrasonic system through electrolysis. GC and TLC were employed to monitor electrolysis progress. GC samples were taken, after every 0.5 equivalent of electron was consumed, from the anodic compartment by 10 µL syringe. TLC was run in solvent systems as indicated. After allowed time was reached, the electrolysis was stopped, and the anodic solution was then transferred into a suitable flask for work-up. The products were separated by flash column chromatography (or preparative TLC) and characterized by NMR, IR, MS and other methods.

7.1.3 Materials and Purification

LiClO₄, LiBF₄ and n-Bu₄NPF₆ were purchased from Aldrich and were dried under vacuum before use. (NH₄)₂Ce(NO₃)₆ (Aldrich) was dried under vacuum before use. CH₃CN (Mallinckrodt, HPLC grade, 99+ %) was stirred over calcium hydride (Aldrich) until the cessation of gas evolution, refluxed over calcium hydride at least one hour, then distilled slowly, discarding the first 5 and last 10 % of distillate. CH₃OH (Baker Analyzed HPLC) was dried by stirring over calcium hydride, followed by distillation before use.
CH$_2$Cl$_2$ was refluxed with P$_2$O$_5$ and distilled before use. Argon was dried and purified according to reference. THF was distilled from LiAlH$_4$ before use.

The following reagents for synthesis and reactions were purchased and used without purification: cyclopropylbenzene, toluene, 1-methylnaphthalene, 9,10-dimethylanthracene, anthrone, Mg, cyclopropylbromide, NBS, Br$_2$, CH$_3$Li, CH$_3$I, 1-bromo-4-methylnaphthalene, acetaldehyde, ethyl iodide, methylene iodide, and other common solvents and inorganic reagents.

7.2 SYNTHESIS OF STARTING MATERIALS

7.2.1 Cyclopropylanthracenes

9-Cyclopropylanthracene.$^{130}$ Cyclopropylmagnesium bromide was prepared by mixing cyclopropylbromide (6.5 mL, 80 mmol) with magnesium turnings (3.0 g, 124 mmol) in 100 mL diethyl ether in the presence of small amount of iodine. A weighed amount of anthrone (14.0 g, 70 mmol) was dissolved in 200 mL THF and the solution was added dropwise to the Grignard reagent. The reaction mixture was refluxed for 3 hours. After cooling to room temperature and chilling in an ice-bath for 10 min, the resulting solution was gradually acidified with concentrated HCl and extracted with CH$_2$Cl$_2$/H$_2$O. The combined extracts were washed with saturated solution of sodium bisulfate and dried over anhydrous sodium sulfate. Crude product was obtained by percolating the product through a column of neutral alumina with hexane-dichloromethane (95:5, v/v). After a second column separation, 4.91g 9-cyclopropylanthracene was obtained and large amount
Chapter 7. Experimental

of anthrone was recovered. The yield of product was not calculated. Pure product was obtained by recrystallization from ethanol. Melting point of the product is 133→135 °C (literature 133→135 °C).154

9-Bromo-10-cyclopropylanthracene.154 A 200 mL carbon tetrachloride solution of bromine (0.53 mL, 10.3 mmol) was added dropwise using an addition funnel to a mixture of 9-cyclopropylanthracene (4.5 g, 10.3 mmol) and NBS (1.76 g, 10.3 mmol) in a 500-mL round bottom flask wrapped with aluminum foil and equipped with a magnetic stirring bar. The reaction mixture was maintained at 15 °C in a water bath. After 1 hour, 200 mL aqueous solution of sodium bisulfite was added to quench the reaction. The organic layer was isolated, dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The resulting residue was dissolved in 40 mL of hexane, chilled in an ice-bath and filtered to further remove any unreacted NBS and the corresponding succinimide that formed. After column chromatography, using neutral alumina soaked in hexane as a stationary phase and dual-solvent benzene-hexane (1:30, v/v) as a mobile phase, 9-bromo-10-cyclopropylanthracene was isolated. Recrystallization from ethanol afforded 3.26 g yellow crystal of 9-bromo-10-cyclopropylanthracene. The melting point of product was 112→113°C (literature 113→114°C).154

9-Cyclopropyl-10-methylanthracene. 1.0 g (3.4 mmol) of 9-bromo-10-cyclopropylanthracene (vacuum-dried) was added to flame-dried 250 mL round-bottomed flask fitted with stirrer and under nitrogen. 50 mL THF was then introduced into flask. 3 mL 1.4 M CH₃Li solution (4.2 mmol CH₃Li) was added via syringe dropwise to the
solution. The color of solution turned into dark yellow green immediately. 1 mL CH$_3$I was added to complete the reaction. The reaction mixture was stirred for one hour and then poured into water. The organic compounds were extracted with diethyl ether from water, dried over anhydrous MgSO$_4$ and concentrated. Recrystallization in ethanol yielded 0.6 g (76%) solid 9-cyclopropyl-10-methylanthracene.

**9-Cyclopropyl-10-methylanthracene**  
$^1$H NMR $\delta$ 0.79(2H, m), 1.46(2H, m), 2.49(1H, m), 3.11(3H, s), 7.52(4H, m), 8.32(2H, d), 8.81(2H, d); $^{13}$C NMR $\delta$ 9.7(CH$_2$), 10.6(CH$_3$), 14.1(CH), 124.4(CH, aromatic), 124.7(CH, aromatic), 125.1(CH, aromatic), 126.6(CH, aromatic), 129.6(C, aromatic), 129.9(C, aromatic), 131.4(C, aromatic), 133.2(C, aromatic); IR (CHCl$_3$) $\nu$ 3085, 3002, 1461(s), 1026(s), 875;

MS(EI) $m/e$ 232(M$^+$, 80), 217(M-CH$_3$, 100); HRMS(EI) for C$_{18}$H$_{16}$, expt’l 232.1262, calc. 232.1252, error 4.4 ppm.

7.2.2 Cyclopropynaphthalenes

**1-Cyclopropynaphthalene.** The synthesis of 1-cyclopropynaphthalene from 1-bromonephthalene was accomplished under literature’s procedures.

**1-Bromo-3-naphthylpropane.** A Grignard reagent was prepared by mixing 1-bromonaphthalene (13 mL) and Mg turnings (4.12 g) in 100 mL THF in the presence of 1,2-dibromoethane (initiator). Into a 500mL three-neck flask was added 0.35 g pre-dried CuBr, 9.5 mL HMPA, 10 mL 1,3-dibromopropane and 20 mL THF. The reaction mixture was heated to reflux, and the Grignard reagent was then added dropwise. After all Grignard reagent was added, the solution was kept to reflux for three hours. When reaction was completed, the reaction mixture was poured into a 100 mL ice-HCl solution
and extracted with benzene/H$_2$O. The extracts was washed with H$_2$O, NaOH (10%) solution and H$_2$O again, dried over Mg$_2$SO$_4$ and evaporated to dryness.

The dark green oily liquid obtained from above was subject to Kuaelrohr distillation. The second portion of distillate (8.3 g, boiling point range: 115→195°C at 2→3 mmHg) was collected. $^1$H NMR and GC showed impurities like 1,3-dibromopropane, HMPA and dimers existed and only ~50% of 1-bromo-3-naphthylpropane was in distillate. Short-path distillation was needed to further separate the product. The distillate in the temperature range of 145→150 °C (0→1 mmHg) was collected and 3.4 g (80% purity) of 1-bromo-3-naphthylpropane was obtained.

1,3-Dibromo-3-naphthylpropane. A mixture of 2.7 g (10.8mmol) 1-bromo-3-naphthylpropane, 3.36 g(13.6 mmol) NBS, 0.15 g (PhCO$_2$)$_2$ and 50 mL CCl$_4$ was refluxed in a dry 250 mL three-neck flask fitted with water condenser circulated with nitrogen. GC was employed to monitor reaction progress (monitoring appearance of starting material). More NBS was added if reaction was not complete. After all starting material was consumed, the reaction mixture was cooled to room temperature, filtered, and concentrated. The resulting dark brown oil contained 1,3-dibromo-3-naphthylpropane as only major product.

1-Cyclopropylnaphthalene. Preparation of zinc-copper couple was described elsewhere.$^{156}$ Zn-Cu couple (3.0 g) was transferred into 250 mL flask with 50 mL THF. A 30 mL of 1,3-dibromo-3-naphthylpropane THF solution was added to the flask with stirring at 0 °C. After addition the reaction mixture was heated to 40 °C and GC was used to monitor the reaction progress. After all starting material was consumed, the solution was filtered and extracted with ether/H$_2$O for several times. The ether layer was dried
Chapter 7. Experimental

over MgSO₄ and evaporated. The resulting yellow brown liquid was subject to short-path distillation, which yielded 1.0 g (85% purity) of 1-cyclopropynaphthalene. Further purification was completed by column chromatography.

**1-Bromo-4-cyclopropynaphthalene.** A mixture of 1-cyclopropynaphthalene (0.85 g, 5 mmol), K₂CO₃ (0.85 g), Fe dust (0.2 g) and 100 mL CCl₄ was stirred in 250 mL three-neck flask. A solution of Br₂ (0.85 g, 0.28 mmol) and 50 mL CCl₄ was added dropwise. The reaction mixture was stirred under dark (covered with Aluminum foil). More Br₂ was added if reaction was not complete based on GC monitoring. After all starting material was converted, the solution was worked up with H₂O. The CCl₄ layers were combined, dried over MgSO₄ and concentrated. The resulting green dark oil contained 86% 1-Bromo-4-cyclopropynaphthalene. Column chromatography using hexane as eluting solvent gave 1.2 g (~93% purity) 1-bromo-4-cyclopropynaphthalene.

**2-Cyclopropynaphthalene.** Synthesis of 2-cyclopropylanthracene followed the procedures by which 1-cyclopropynaphthalene was synthesized.

**1-Cyclopropyl-4-methylnaphthalene.**

**1-(4-methylnaphthyl)ethanol.** In a 500 mL three-necked round-bottomed flask fitted with magnetic stirrer and water condenser and circulated with nitrogen was added 4.32 g magnesium (180 mmol). 150 mL THF was added to flask via syringe. The solution was stirred and warmed (~30 °C). 14.2 g (60 mmol) 1-bromo-4-methylnaphthalene was then added gradually through syringe. Reaction was observed and
controlled by adjusting temperature (30→40 °C) or addition rate of 1-bromo-4-methylnaphthalene. After all reagent was added, the reaction mixture was heated under reflux for one additional hour and then cooled to room temperature.

Into the flask of Grignard reagent prepared above was added gradually 5 mL (3.94 g, 90 mmol) acetaldehyde (caution: reaction occurs rapidly and releases heat). The mixture was stirred at room temperature for about one hour. The resulting solution was poured into 20% H$_2$SO$_4$ aqueous solution. A 100 mL diethyl ether was added, and the ether layer was separated, washed with water, 10% NaOH solution and water again, dried over anhydrous MgSO$_4$, filtered and concentrated. The crude 1-(4-methylnaphthyl)ethanol was kept in refrigerator overnight. The alcohol crystal thus formed was filtered and washed with hexane. The filtrate was concentrated and the remained alcohol was separated by column (silica gel) with dichloromethane as eluting solvent. The total 1-(4-methylnaphthyl)ethanol (solid) separated weighted 12.7g (95%).

**TLC** (CH$_2$Cl$_2$) $R_f = 0.24$; **$^1$H NMR** $\delta$ 1.55(3H, d), 2.38(1H, s), 2.60(3H, s), 5.49(1H, q), 7.21(1H, d), 7.47(3H, m), 7.98(2H, m).

**1-Methyl-4-vinylnaphthalene.** Into a 250mL round-bottomed flask fitted with magnetic stirrer and nitrogen flowing adapter was added 10.0 g (54 mmol) 1-(4-methylnaphthyl)ethanol. The flask was stirred and heated under nitrogen flow. After solid alcohol was melted, the flask was kept at a temperature of 60→70 °C for about 10 minutes. Tiny water drops was observed formed on the surface of the flask. The reaction was stopped by removing heater, based on reaction progress monitored by GC. Besides the desired product 1-methyl-4-vinylnaphthalene, a huge amount of polymer was formed and some starting material left unreacted. The resulting reaction mixture was worked up
with diethyl ether and water. The organic layer was separated, dried over anhydrous MgSO₄, filtered and concentrated. Column separation with hexane as eluting solvent yielded 1.92 g (23.2%) liquid 1-methyl-4-vinyl napthalene. \textbf{TLC} (hexane) \( R_f = 0.46; \) \[\textbf{H NMR} \delta 2.67(3H, s), 5.41(1H, d), 5.73(1H, d), 7.27(1H, d), 7.44(1H, q), 7.50(3H, m), 7.99(1H, m), 8.11(1H, m); \) \[\textbf{C NMR} \delta 19.6(\text{CH}_3), 116.4(=\text{CH}_2), 123.4(\text{CH}, \text{aromatic}), 124.3(\text{CH}, \text{aromatic}), 124.6(\text{CH}, \text{aromatic}), 125.6(\text{CH}, \text{aromatic}), 125.7(\text{CH}, \text{aromatic}), 126.5(\text{CH}, \text{aromatic}), 131.2(\text{C}, \text{aromatic}), 132.6(\text{C}, \text{aromatic}), 134.1(\text{C}, \text{aromatic}), 134.4(\text{C}, \text{aromatic}), 134.6(=\text{CH}-); \) \[\textbf{GC-MS(El)} m/e 169(M+1, 7), 168(M, 49), 153(M-\text{CH}_3, 100). \]

\textit{1-Cyclopropyl-4-methylnapthalene.} 100 mL stock solution of ethylzinc iodide was prepared in the following procedure: Ethyl iodide (17.3 g, 0.11 mol) was allowed to react with zinc-copper couple II (7.5 g, 0.11 mol), which was prepared previously, and the mixture was stirred at room temperature overnight. The supernatant liquid was withdrawn free from sludge and stored in a stoppered flask carrying a drying tube. After storage at room temperature for one week no precipitate was formed, and the activity of the solution remained unchanged.

Methylene diiodide (3.5 g, 0.013 mol) was added to an aliquot of the stock solution (25 mL) containing about 0.5 equivalents of ethylzinc iodide and the mixture was stirred at reflux (30 ℃) for one hour (the reaction releases heat when adding methylene iodide to ethylzinc iodide solution). To the chilled solution, 1.9 g (0.0113 mol) 1-methyl-4-vinyl napthalene was added, and the mixture was stirred and heated under reflux (30→40 ℃). After 15 hours, starting 1-methyl-4-vinyl napthalene was all consumed and 1-cyclopropyl-4-methylnapthalene was produced, monitored by GC. The reaction
mixture was quenched with water and dilute HCl (10%), extracted with water and diethyl ether, and the ether layer was washed with water, NH₄NO₃ aqueous solution and again water, dried over anhydrous MgSO₄ and concentrated. The crude product (liquid) was subjected to column separation with hexane as eluting solvent, which yielded 2.0 g (97%) 1-cyclopropyl-4-methylnaphthalene.

**1-Cyclopropyl-4-methylnaphthalene**  
**TLC** (hexane) Rₙ = 0.43;  
**¹H NMR** δ 0.84(2H, m), 1.12(2H, m), 2.38(1H, m), 2.75(3H, s), 7.26(1H, d), 7.30(1H, d), 7.64(2H, m), 8.10(1H, d), 8.54(1H, d);  
**¹³C NMR** δ 6.4(CH₂), 13.4(CH), 19.5(CH₃), 123.8(CH, aromatic), 124.7(CH, aromatic), 125.1(CH, aromatic), 125.4(CH, aromatic), 125.5(CH, aromatic), 126.3(CH, aromatic), 132.0(C, aromatic), 132.7(C, aromatic), 133.6(C, aromatic), 137.3(C, aromatic);  
**IR** (CHCl₃) ν 3071, 3006, 1597, 1512, 1217, 1112, 1023, 907;  
**MS(EI)** m/e 183(M+1, 3.5), 182(M⁺, 27), 167(M-15, 100), 152(49), 141(11);  
**HRMS(EI)** C₁₄H₁₄, calc. 182.1096, expt’l. 182.1100, error 2.7 ppm.

### 7.2.3 1-Cyclopropyl-4-methylbenzene

**Zinc-Copper Couple.** In a 500 mL Erlenmeyer flask fitted with a magnetic stirrer was placed zinc powder (49.2 g, 0.75 mol) and 40 ml of 3% hydrochloric acid. The mixture is stirred rapidly for 1 minute, then the supernatant liquid is decanted. In a similar manner the zinc powder is washed successively with three additional 40 mL portions of 3% hydrochloric acid, five 100 mL portions of distilled water, two 75 mL portions of 2% aqueous copper sulfate solution, five 100 mL portions of distilled water, four 100 mL portions of absolute ethanol, and five 100 mL portions of absolute ether. The couple is finally transferred to a Buchner funnel, washed with additional anhydrous ether, covered
tightly with a rubber dram, and suction-dried until it reaches room temperature. The zinc-copper couple is vacuum-dried at 40 °C for overnight and is then ready for use.

**1-Cyclopropyl-4-methylbenzene.** In a 250 mL round-bottomed flask fitted with magnetic stirrer and water condenser protected by nitrogen adapter are placed 3.1 g Zn-Cu couple and 25 mL diethyl ether. A 5mL mixture of 1-methyl-4-vinylbenzene (3.54 g, 30 mmol) and diiodomathane (8.8 g, 33 mmol) in diethyl ether is then added gradually. The reaction mixture is stirred and heated under reflux. GC was employed to monitor reaction progress and after 27 hours, reaction is stopped. The resulting mixture is poured into 30 mL saturated ammonium chloride aqueous solution. The organic layer is separated, washed with saturated NaHCO₃ solution then distilled water for several times, dried over anhydrous MgSO₄, and concentrated. Fraction distillation under vacuum (43→49 °C, ~3 mmHg) affords 1.8 g (45%) liquid 1-cyclopropyl-4-methylbenzene (91% purity). ¹H NMR δ 0.60(2H, m), 0.85(2H, m), 1.80(1H, m), 2.24(3H, s), 6.90(2H, d), 7.00(2H, d); ¹³C NMR δ 8.9(CH₂), 15.0(CH), 21.0(CH₃), 125.6(CH, aromatic), 128.5(CH, aromatic), 134.8(C, aromatic), 140.8(C, aromatic).

### 7.3 ELECTROLYSIS OF CYCLOPROPYLARENES

#### 7.3.1 Cyclopropylanthracenes

**9-Bromo-10-cyclopropylanthracene.** 56.0 mg (0.189 mmol) of 9-bromo-10-cyclopropylanthracene in CH₃CN containing 2.5 M methanol was electrolyzed at -30 mA for 27 min (2.7 equiv. e⁻’s). The anodic solution (30 mL) was divided into two portions.
and two work-up procedures were employed. Analogous procedures were followed for electrolyses in the presence of 4.1 and 0.25 M CH$_3$OH. The results are summarized in Table 4-4.

*Aquous Workup.* One portion of electrolytic solution was extracted with H$_2$O/ether 3x. The ether layers were combined, dried with MgSO$_4$ (Mallinckrodt), and evaporated. CDCl$_3$ was then added to the flask to dissolve the residue. The CDCl$_3$ solution was filtered and transferred to an NMR tube. After addition of an internal standard [(CH$_3$)$_3$SiOSi(CH$_3$)$_3$], $^1$H NMR was used to determine the yield of 9-cyclopropyl-9-methoxynanthrone. An analytical sample of 9-cyclopropyl-9-methoxynanthrone was obtained for characterization via flash column chromatography with CH$_2$Cl$_2$ as solvent:

**9-Cyclopropyl-9-methoxynanthrone**  
TLC $R_f$ = 0.42 (CH$_2$Cl$_2$);  
$^1$H NMR $\delta$ 0.304(m, 2H, trans-cyclopropylmethene), 0.334(m, 2H, cis-cyclopropylmethylene), 1.20(m, 1H, cyclopropylmethine), 2.99(s, 3H, methyl), 7.94(t, 2H, aromatic), 7.67(t, 2H, aromatic), 7.76(d, 2H, aromatic), 8.29(d, 2H, aromatic);  
$^{13}$C NMR $\delta$ 2.44(t, CH$_2$), 28.1(d, CH), 52.3(q, OCH$_3$), 77.6(s), 126.7(d, aromatic), 127.3(d, aromatic), 127.9(d, aromatic), 132.1(s, aromatic), 133.1(s, aromatic), 144.2(s, aromatic), 183.4(s, C=O);  
IR $\nu$ 1665(s, C=O), 1601(s), 1458(m), 1319(s), 1272(s), 1072, 911, 819, 738, 652;  
MS(EI) $m/e$ 265(M$^+$, 3.38), 264(M$^+$, 18.7), 249(3), 236(M-28, 92), 223(M-cyclopropyl, 100), 215(17.8), 208(15.3), 202(20), 193(33.8), 165(84.6), 152(48.8);  
HRMS(EI) for C$_{18}$H$_{16}$O$_2$, calcd. 264.1150, exptl 264.1158, error 2.9 ppm.
**Non-aqueous Workup.** The second portion of the electrolytic solution was transferred into a 50 mL flask and evaporated. CH$_2$Cl$_2$ was added to extract the organic materials, and the resulting solution filtered to remove LiClO$_4$. Yields of products were determined by $^1$H NMR analysis. Analytical samples of these compounds were obtained as follows: Flash column chromatography of the non-aqueous work-up solution with CH$_2$Cl$_2$ as eluting solvent gave pure ring opened product methoxy ether, and a mixture of ring opened perchlorate ester and bromide, which were subsequently separated via flash chromatography using a solvent gradient 5 → 20% EtOAc/hexane.

**Methoxy Ether**

TLC: $R_f = 0.14$ (CH$_2$Cl$_2$), 0.15 (hexane/CH$_2$Cl$_2$/EtOAc = 14:5:1); $^1$H NMR $\delta$ 2.95(q, 2H, J=6.5Hz), 3.38(s, 3H, OCH$_3$), 3.59(t, 2H, J=6.3Hz), 6.62(t, 1H, J=7.08Hz), 7.26~7.50(m, 2H), 7.53~7.64(m, 2H), 7.76~7.85(q, 2H); $^{13}$C NMR $\delta$ 31.7(t, C$_2$H), 58.8(q, OCH$_3$), 71.9(t, CH$_2$OCH$_3$), 123.5(d), 126.8(d), 127.3(d), 127.4(d), 127.7(d), 127.8(d), 130.3(s), 131.7(d), 132.1(s), 132.2(s), 132.8(d), 133(d, CH), 136.8(s), 141.1(s), 184.8(s, C=O); IR $\nu$ 1665(s, C=O), 1598(s), 1320(s), 1122, 912.5, 939; MS (EI) $m/e$ 265(M+1, 7), 264(M$^+$, 32.7), 249(M-CH$_3$, 5.4), 231(19), 230(37), 219(M-CH$_2$OCH$_3$, 100), 202(32), 189(38), 165(24.6), 45(CH$_2$OCH$_3^+$, 91), 15(CH$_3^+$, 9); HRMS (EI) for C$_{18}$H$_{16}$O$_2$: calc. 264.1150, expt'l 264.1146, error -1.6 ppm.

**Perchlorate Ester**

M.P.: 98 - 99 °C; TLC $R_f = 0.34$ (CH$_2$Cl$_2$), 0.15 (hexane/EtOAc = 4:1), 0.15 (hexane/CH$_2$Cl$_2$/EtOAc = 14:5:1); $^1$H NMR $\delta$ 3.20 (q, 2H, J = 7 Hz), 4.73 (t, 2H, J = 7 Hz), 6.42 (t, 1H, J = 7 Hz), 7.50 - 7.66 (m, 5H), 7.80 (d, 1H), 8.28 (q, 2H); $^{13}$C NMR $\delta$ 29.2 (t, CH$_2$), 74.4 (t, CH$_2$OCIO$_3$), 123.4 (d), 127.0 (d), 127.3
(d, CH), 127.7 (d), 128.1 (d), 128.5 (d), 130.5 (s), 131.9 (d), 132.3 (s), 133.1 (d), 134.6 (s), 136.1 (s), 140.4 (s), 184.5 (s, C=O); \textbf{IR} \nu 1664 (s, C=O), 1598 (s), 1474, 1382, 1317, 1289, 1269 (s, \nu_3 \text{ClO}_3), 1235 (s, \nu_2 \text{ClO}_3), 1098, 1037 (s, \nu_3 \text{ClO}_3); \textbf{MS(CI)} \textit{m/e} 287 (MH$^+$ + 2 - O$_3$, 0.5), 285 (MH$^+$ - O$_3$, 1.5), 251 (MH$^+$ + 2 - ClO$_3$, 7.5), 249 (MH$^+$ - ClO$_3$, 5.4), 233 (MH$^+$ - ClO$_4$, 22.8), 231 (33.6), 221 (17.4), 209 (24), 195 (100), 194 (96.6), 165 (19.5); \textbf{MS(FAB)} \textit{m/e} 335 (MH$^+$ + 2, 17.4), 333 (MH$^+$, 48.6), 273 (13.2), 251 (MH$^+$ + 2 - ClO$_3$, 16.5), 233 (MH$^+$ - ClO$_4$, 19.8), 231 (22.2), 220 (48.6), 219 (40.8), 83 (ClO$_3^+$, 34.2), 73 (65.4), 69 (HClO$_2^+$, 56.4), 55 (100); \textbf{HRMS} (Cl) for C$_{17}$H$_{14}$O$_5$Cl (MH$^+$), calc. 333.0529, expt’l 333.0512, error -5.0 ppm; \textbf{Elemental Analysis} (Atlantic Microlab, Inc.) for C$_{17}$H$_{13}$O$_5$Cl, calc. C 61.44, H 3.95, expt’l C 60.63, H 4.21.

\textbf{Bromide: TLC} \textit{R}_f = 0.34 (CH$_2$Cl$_2$), 0.24(hexane/EtOAc = 4:1); \textbf{^1H NMR} \delta 3.26 (q, 2H, J = 7 Hz), 3.57 (t, 2H, J = 7 Hz), 6.54 (t, 1H, J = 7 Hz), 7.45 - 7.56 (m, 2H), 7.59 - 7.68 (m, 3H), 7.83 (d, 1H), 8.28 (q, 2H); \textbf{^13C NMR} \delta 31.9 (t, CH$_3$), 33.95 (t, CH$_2$Br), 126.9 (d), 127.4 (d), 127.5 (d), 127.7 (d), 128.2 (d), 133.0 (s), 130.4 (s), 131.8 (d), 132.2 (s), 132.24 (d, CH), 132.5 (d), 132.9 (d), 136.6 (s), 140.7 (s), 184.6 (s, C=O); \textbf{IR} \nu 1662 (s, C=O), 1598 (s), 1474 (s), 1383, 1315, 1287, 1098; \textbf{MS(EI)} \textit{m/e} 314 (M + 2, 16.8), 312 (M$^+$, 16.5), 233 (40.8), 231 (25.8), 219 (45.6), 215 (100), 202 (39), 189 (39.6), 165 (20.4); \textbf{MS(CI)} \textit{m/e} 343 (M + 2 + C$_2$H$_5^+$, 7.5), 341 (M + C$_2$H$_5^+$, 6.3), 315 (MH$^+$ + 2, 40.8), 313 (MH$^+$, 26.4), 261 (7.8), 263 (13.2), 235 (63), 233 (100); \textbf{HRMS} (EI) for C$_{17}$H$_{13}$BrO, calc. 312.0150, expt’l 312.0139, error -3.4 ppm.

\textbf{9-Cyclopropylanthracene.} 47.6 mg (0.218 mmol) of 9-cyclopropylanthracene in CH$_3$CN containing 2.5 M CH$_3$OH was electrolyzed at -30 mA for 35 min (3.0 equiv. e$^-$).
Portions of the reaction mixture were subjected to aqueous and non-aqueous workup (vide supra) and quantitative $^1$H NMR analysis. The results of this and other analogous runs are summarized in Table 4-5.

50.5 mg (0.232 mmol) of 9-cyclopropylanthracene was electrolyzed at -30 mA for 25 min. (2.0 equiv. e$^-$'s). The progress of the electrolysis was monitored by GC and TLC (3 : 1 hexane : CH$_2$Cl$_2$) so as to stop the electrolysis when the yield of 9-cyclopropyl-10-methoxyanthracene was maximal. The anodic solution (30ml) was extracted with ether and water several times, dried (MgSO$_4$), and evaporated. Yields (based upon $^1$HNMR analysis are summarized in Table 4-5. Flash column chromatography with a solvent gradient starting at 0% and finishing at 25% CH$_2$Cl$_2$/hexane yielded 18% (10.4 mg) of 9-cyclopropyl-10-methoxyanthracene.

**9-Cyclopropyl-10-methoxyanthracene**  
$^1$H NMR $\delta$ (assignments with aid of 2D NMR), 0.80 (m, 2H, cis-cyclopropyl methylene hydrogens), 1.44 (m, 2H, trans-cyclopropyl methylene hydrogens), 2.43(m, 1H, cyclopropyl methine hydrogen), 4.14 (s, 3H, CH$_3$O), 7.46 - 7.55 (m, 4H, 2-, 3-, 6-, and 7-anthryl hydrogens), 8.34 (m, 2H, 1- and 8-anthryl hydrogens), 8.77 (m, 2H, 2- and 4-anthryl hydrogens).  
$^{13}$C NMR $\delta$ (adept assignment) 9.3 (t, CH$_2$), 10.2 (d, CH), 63.2 (q, OCH$_3$), 122.6 (d), 124.2 (s), 124.7 (d), 125.1 (d), 126.3 (d), 130.7 (s), 132.3 (s), 151.7 (s).  
IR $\nu$ 1664, 1620, 1652, 1452, 1390(s), 1330(s), 1282, 1116, 1088, 1027, 971.  
**MS**(EI) $m/e$ 249 (M + 1, 8.5), 248 (M$^+$, 49), 247 (30), 233 (M - CH$_3$, 47), 217 (M - OCH$_3$, 100), 215 (89), 202 (49), 189 (39);  
**HRMS** (EI) for C$_{18}$H$_{16}$O, calc. 248.1201, expt'l 248.1202, error 0.3 ppm.
Control Experiments. A 30 mL CH₃CN solution of 9-cyclopropyl-9-methopxyanthrone (27.7mg) was divided into 3 portions: 1ml CH₃OH (2.5M) and 0.1g (0.1M) LiClO₄ was added to the first portion and the reaction was subsequently subjected to non-aqueous workup. TLC and GC of the resulting solution revealed only unreacted 9-cyclopropyl-9-methopxyanthrone. To the second portion was added 0.1 g LiClO₄ and 1 drop HBr (32%). The reaction mixture was subjected to non-aqueous workup. TLC and GC of resulting solution showed the complete conversion of 9-cyclopropyl-9-methopxyanthrone → bromide. The yield of bromide based on ¹H NMR analysis was 80%. To the third portion was added 0.1 g LiClO₄ and 1 drop of HClO₄ (60-70%). Non-aqueous workup yielded 46% of perchlorate ester based upon ¹H NMR analysis.

7.3.2 Cyclopropynaphthalenes

1-Cyclopropynaphthalene

Run 1. 1-Cyclopropynaphthalene (44 mg, 0.262mmol) in the presence of 2.5 M CH₃OH was electrolyzed at -30 mA for 42 min passing 3.0 equivalents of electrons. The electrolytic solution was worked up with H₂O/diethyl ether. The PTLC of the work-up solution with solvent system of hexane and ethyl acetate (3:1) yielded the following compounds:

1-(1,3-Dimethoxypropyl)naphthalene  TLC (hexane : ethyl acetate = 3 : 1)

Rₜ =0.40; ¹H NMR (CDCl₃) δ 2.13(m, 2H, -CH₂- ), 3.21(s, 3H, -OCH₃ ), 3.35(s, 3H, -OCH₃ ), 3.38(m, 1H, -CH₂-OCH₃ ), 3.60(m, 1H, -CH₂-OCH₃ ), 5.07(t, 1H, >CH-OCH₃), ~7.50(m, 3H, aromatic), 7.55(d, 1H, aromatic), 7.78(d, 1H, aromatic), 7.87(m, 1H, aromatic), 8.22(d, 1H, aromatic); ¹³C NMR (CDCl₃) δ 37.82(t, -CH₂- ), 56.96(q, -
OCH₃), 58.71(q, -OCH₃), 69.42(t, -CH₂-OCH₃), 78.41(d, >CH-OCH₃), 123.44(d, aromatic), 123.82(d, aromatic), 125.45(d, aromatic), 125.48(d, aromatic), 125.89(d, aromatic), 127.89(d, aromatic), 128.80(d, aromatic), 131.15(s, aromatic), 133.90(s, aromatic); IR v 3157, 3062, 2985, 2899, 2827, 1600, 1518, 1475, 1394, 1116(s), 809(s), 785(s); MS (EI) m/e 231(1.52, M+1), 230(7.92, M⁺), 172(13.2, M+1 - -CH₂CH₂OCH₃), 171(100, M - -CH₂CH₂OCH₃), 165(15.2), 128(19.2);


4, 4’-Di(1, 3-dimethoxypropyl)-1, 1’-binaphthalene TLC (hexane : ethyl acetate = 3 : 1) Rf =0.21; ¹H NMR (CDCl₃) δ 2.23(m, 2H, -CH₂-), 3.40(s, 3H, -OCH₃), 3.41(s, 3H, -OCH₃), 3.46(m, 1H, -CH₂-OCH₃), 3.70(m, 1H, -CH₂-OCH₃), 5.18(m, 1H, >CH-OCH₃), 7.29(t, 1H, aromatic), 7.44(d, 1H, aromatic), 7.50(t, 2H, aromatic), 7.67(d, 1H, aromatic), 8.31 (d, 1H, aromatic); ¹³C NMR (CDCl₃) δ 37.91(t, -CH₂-), 57.15(q, -OCH₃), 58.76(q, -OCH₃), 69.49(t, -CH₂-OCH₃), 78.43(d, >CH-OCH₃), 123.27(d, aromatic), 123.52(d, aromatic), 125.50(d, aromatic), 125.75(d, aromatic), 127.46(d, aromatic), 127.55(d, aromatic), 131.15(s, aromatic), 133.28(s, aromatic), 137.50(s, aromatic), 138.25(s, aromatic); IR v 3081, 3047, 2988, 2939, 2904, 2831, 1733, 1670, 1601, 1523, 1474, 1454, 1391, 1303, 1258, 1214, 1175, 1121(s), 857, 778(s); MS (EI) m/e 460(2, M+2), 459(10, M+1), 458(44, M⁺), 427(3, M- -OCH₃), 401(3.6, M+2 - -CH₂CH₂OCH₃), 400(23.2, M+1 - -CH₂CH₂OCH₃), 399(100, M- -CH₂CH₂OCH₃), 427(5), 325(22.4), 252(17.6), 170(8.6); HRMS (EI) C₃₀H₃₄O₄, expt’l 458.2445, cacl 458.2457, error -2.6 ppm.

**Run 2.** 1-Cyclopropynaphthalene (41.1 mg, 0.245 mmol) in the presence of 2.5 M CH₃OH was electrolyzed at -40 mA for 35 min passing 3.5 equivalents of electrons.
The electrolytic solution was worked up with H₂O / diethyl ether. The work-up solution was subject to HPLC analysis, which yielded 2.94 mg (7.45%) of starting material, 9.42 mg (17.43%) of 1-(1,3-dimethoxypropyl)naphthalene, and 14.13 mg (26.27%) of 4,4’-di(1,3-dimethoxypropyl)-1,1’-binaphthalene (HPLC condition: CH₃CN : H₂O = 90% : 10%; flow rate = 1mL/min; λ = 224nm; C₁₈ column).

**1-Bromo-4-cycloproplynnaphthalene**

**Run 1.** 1-bromo-4-cycloproplynnaphthalene (64.6 mg, 0.263 mmol) in the presence of 2.5 M CH₃OH was electrolyzed at -40 mA for 33 min passing 3.0 equivalents of electrons. The electrolytic solution was worked up with H₂O/diethyl ether. The PTLC of the work-up solution with CH₂Cl₂ as solvent yielded:

**1-Bromo-4-(1,3-dimethoxypropyl)naphthalene** 40.8 mg (50.4%), TLC (CH₂Cl₂), Rₛ = 0.44; ¹H NMR (CDCl₃) δ 2.09(q, 2H, -CH₂-), 3.29(s, 3H, -OCH₃), 3.34(m, 1H, -CH₂-OCH₃), 3.35(s, 3H, -OCH₃), 3.61(m, 1H, -CH₂-OCH₃), 5.05(t, 1H, >CH-OCH₃), 7.42(d, 1H, aromatic), 7.58(m, 2H, aromatic), 7.79(d, 1H, aromatic), 8.22(d, 1H, aromatic), 8.31(d, 1H, aromatic); ¹³C NMR (CDCl₃) δ 37.89(t, -CH₂-), 57.06(q, -OCH₃), 58.74(q, -OCH₃), 69.20(t, -CH₂-OCH₃), 78.02(d, >CH-OCH₃), 122.46(s, aromatic C-Br), 123.75(d, aromatic), 124.28(d, aromatic), 126.72(d, aromatic), 126.94(d, aromatic), 127.98(d, aromatic), 129.64(d, aromatic), 132.06(s, aromatic), 132.38(s, aromatic), 138.01(s, aromatic); IR ν 3079, 3045, 2990, 2929, 2892, 2831, 1595, 1571, 1510, 1473, 1448, 1387, 1314, 1257, 1203, 1161, 1118(s), 1014; MS(EI) m/e 310(6.8, M+2), 308(8, M⁺), 252(10), 251(100, M+2 - -CH₂CH₂OCH₃), 249(97.6, M-...
-CH₂CH₂OCH₃), 165(14.8), 153(20.8), 152(38.4), 127(21.2), 126(26), 45(78.4); HRMS (El) C₁₅H₁₇O₂Br, expt’l 308.0410, cacl. 308.0412, error -0.6 ppm.

**Rum 2.** 1-Bromo-4-cyclopropynaphthalene (56.6 mg, 0.230 mmol) in the presence of 2.5 M CH₃OH was electrolyzed at -40 mA for 17.2 min passing 2.0 equivalents of electrons. The electrolytic solution was worked up with H₂O / diethyl ether. The ¹H NMR analysis of the work-up solution yielded 56.7 mg (80%) of 1-bromo-4-(1, 3-dimethoxypropyl)naphthalene, and GC analysis showed 7.5 mg (13.2%) of starting material left unreacted.

**2-Cyclopropynaphthalene.** 2-Cyclopropynaphthalene (82.2 mg, 0.49 mmol) in the presence of 5.0 M CH₃OH was electrolyzed at -60 mA for 27 min passing 2.0 equivalents of electrons. The electrolytic solution was worked up with H₂O/diethyl ether. The PTLC of the work-up solution with hexane : ethyl acetate = 3:1 as solvent system yielded 18.2 mg (16.2%) 2-(1, 3-dimethoxypropyl) naphthalene, and a mixture of 2, 2’-dicyclopopyl-1, 1’-binaphthalene and starting material. Second PTLC of the mixture with hexane as the solvent gave 14.3 mg (17.5%) of 2, 2’-dicyclopopyl-1, 1’-binaphthalene. Unreacted starting material was estimated from GC analysis was 28 mg (34.1%).

**2-(1, 3-Dimethoxypropyl)naphthalene** TLC (hexane : ethyl acetate = 3:1)
Rᵳ = 0.41; ¹H NMR (CDCl₃) δ 1.95(hexalet, 1H, -CH₂-), 2.17(hexalet, 1H, -CH₂-), 3.25(s, 3H, -OCH₃), 3.33(m, 1H, -CH₂-OCH₃), 3.34(s, 3H, -OCH₃), 3.51(m, 1H, -CH₂-OCH₃), 4.46(t, 1H, >CH-CH₃), ~7.47(m, 3H, aromatic), 7.74(s, 1H, aromatic), ~7.85(m, 3H, aromatic); ¹³C NMR (CDCl₃) δ 38.01(t, -CH₂-), 56.75(q, -OCH₃), 58.65(q, -OCH₃),
Chapter 7. Experimental

69.15(t, -CH$_2$-OCH$_3$), 80.81(d, >CH-OCH$_3$), 124.36(d, aromatic), 125.79(d, aromatic), 125.86(d, aromatic), 125.86(d, aromatic), 126.08(d, aromatic), 127.70(d, aromatic), 127.83(d, aromatic), 128.36(d, aromatic), 133.10(s, aromatic), 133.23(s, aromatic), 139.38(s, aromatic); IR $\nu$ 3156, 3064, 2984, 2935, 2897, 2825, 1473, 1387, 1112(s), 824, 760; MS(EI) $m/e$ 231(3, M+1), 230(15, M$^+$), 215(1.5, M-15), 171(100, M-59), 155(20), 141(15); HRMS (EI) C$_{15}$H$_{18}$O$_2$, expt’l 230.1300, cacl. 230.1307, error -2.8 ppm.

2, 2’-Dicyclopropyl-1, 1’-binaphthalene TLC (hexane) R$_f$ =0.36; $^1$H NMR(CDC$_3$) $\delta$ ~0.60(m, 1H, cyclopropyl-CH$_2$), ~0.74(m, 3H, cyclopropyl-CH$_2$), 1.53(m, 1H, cyclopropyl-CH), ~7.10(m, 2H, aromatic), ~7.21(m, 1H, aromatic), ~7.38(m, 1H aromatoc), ~7.87(m, 2H, aromatic); $^{13}$C NMR (CDCl$_3$) $\delta$ 8.46(t, cyclopropyl-CH$_2$), 9.07(t, cyclopropyl-CH$_2$), 13.38(d, cyclopropyl-CH), 121.43(d, aromatic), 124.76(d, aromatic), 126.04(d, aromatic), 126.06(d, aromatic), 127.71(d, aromatic), 127.85(d, aromatic), 131.81(s, aromatic), 133.02(s, aromatic), 135.01(s, aromatic), 139.85(s, aromatic); IR $\nu$ 3156, 3082, 3058, 3008, 2954, 2923, 2856, 1626, 1595, 1510, 1467, 1381, 1332, 1100, 1045; MS(EI) $m/e$ 335(30, M-1), 334(100, M), 319(20), 305(40), 289(30), 278(40), 277(40), 276(50), 265(30), 263(25); HRMS (EI) C$_{26}$H$_{22}$, expt’l 334.1719, cacl. 334.1722, error -0.6 ppm.

7.4 CAN OXIDATION OF CYCLOPROPYLARENES

7.4.1 Cyclopropylbenzenes
Into 3 vials were introduced 100 uL 1-cyclopropyl-4-methylbenzene (80 mg, 0.6 mmol), cyclopropylbenzene (94 mg, 0.8 mmol) and toluene (86 mg, 0.94 mmol), respectively. 5 mL CH$_3$CN was then added to each vial fitted with stirrer. To each solution, two equiv. of CAN was introduced (660 mg, 877 mg and 1030 mg, respectively). The three vials were put in the electrical plate and heated at a temperature of 75→80 °C for 5 minutes with stirring. For cyclopropane derivatives, the white solid (Ce(III) salt) was gradually formed, but for toluene, no obvious reaction occurred (orange color was not changed).

The reaction mixture was poured into a 30 mL diethyl ether and worked up with water for four times, then the organic layer was dried over MgSO$_4$, filtered and concentrated. 1 mL CDCl$_3$ was added to rinse the products. After addition of certain amount of internal standard, (CH$_3$)$_3$OSiO(CH$_3$)$_3$, $^1$H NMR was run to determine the yields of products.

The product mixture was then separated via preparative thin layer chromatography. For cyclopropylbenzene, PTLC using hexane/ethyl acetate (10:1) as solvent gave pure 1-phenylpropyl-1,3-dinitrate and a mixture of 1-cyclopropyl-2-nitrobenzene and 1-cyclopropyl-4-nitrobenzene, which was in turn separated with PTLC using hexane/CHCl$_3$ (2:1) as solvents. For 1-cyclopropyl-4-methylbenzene, PTLC using hexane/ethyl acetate (10:1) as solvent gave 1-(4-methylphenyl)propyl-1,3-dinitrate and 1-cyclopropyl-2-nitro-4-methylbenzene. It was noted that 1,3-dinitrates can be converted to 1-(4-methylphenyl)-1-hydroxypropynitrate if left on the PLC plate for a long time.

The products were characterized as the following:
1-Phenylpropyl-1,3-dinitrate (60.7%)  $^1$H NMR δ 2.24(1H, m), 2.43(1H, m), 4.42(1H, m), 4.58(1H, m), 5.9(1H, t), 7.40(5H, m); $^{13}$C NMR δ 31.9(CH$_2$), 68.4(CH$_2$), 81.3(CH), 126.3(CH, aromatic), 129.1(CH, aromatic), 129.5(CH, aromatic), 136.4(C, aromatic); IR ν (cm$^{-1}$) 1637(s), 1278(s), 852(s); MS(El) m/e 242(M$^+$, 2.6), 180(M-ONO$_2$, 15.2), 152(14.3), 150(25), 117(32), 105(100); HRMS(EI) C$_9$H$_{10}$O$_6$N$_2$, calc. 242.0539, expt'l 242.0537, error -0.9 ppm.

1-Cyclopropyl-2-nitrobenzene (20%)  $^1$H NMR δ 0.71(2H, m), 1.05(2H, m), 2.39(1H, m), 7.15(1H, d), 7.28(1H, t), 7.47(1H, t), 7.79(1H, d); $^{13}$C NMR δ 8.0(CH$_2$), 12.4(CH), 124.0(CH, aromatic), 126.3(CH, aromatic), 127.9(CH, aromatic), 132.5(CH, aromatic), 138.0(C, aromatic); IR ν (cm$^{-1}$) 1524(s), 1350(s); MS(Cl) m/e 164(MH$^+$, 30), 134(77), 83(100).

1-Cyclopropyl-4-nitrobenzene (7.5%)  $^1$HN MR δ 0.82(2H, m), 1.13(2H, m), 1.99(1H, m), 7.15(2H, d), 8.11(2H, d); $^{13}$C NMR δ 11.0(CH$_2$), 15.8(CH), 123.6(CH, aromatic), 125.9(CH, aromatic), 152.6(C, aromatic); IR ν 1637, 1602, 1519(s), 1340(s); MS(CI) m/e 164(MH$^+$, 11.3); MS(El) 163(M$^+$, 23), 115(100); HRMS(CI) C$_9$H$_{10}$O$_2$N$_1$, calc. 164.0712, expt'l 164.0715, error 2.0 ppm.

1-(4-Methylphenyl)propyl-1,3-dinitrate (67.4%)  $^1$H NMR δ 2.21(1H, m), 2.37(3H, s), 2.41(1H, m), 4.41(1H, m), 4.56(1H, m), 5.88(1H, t), 7.23(4H, dd); $^{13}$C NMR δ 21.2(CH$_3$), 31.8(CH$_2$), 68.5(CH$_2$), 81.4(CH), 126.4(CH, aromatic), 129.8(CH, aromatic), 133.3(C, aromatic), 139.6(C, aromatic); IR(CHCl$_3$) ν 1641(s), 1602, 1519(s), 1216, 908, 849; MS(El) m/e 256(M$^+$, 2.6), 194(M$^+$-ONO$_2$, 1.3), 164(7.8), 119(100); HRMS(El) C$_{10}$H$_{12}$O$_6$N$_2$, calc. 256.0695, expt'l 256.0705, error 3.7 ppm.
1-Cyclopropyl-2-methyl-4-nitrobenzene (12.8%) \(^1\)H NMR \(\delta\) 0.65(2H, m), 1.00(2H, m), 2.34(1H, m), 2.36(3H, s), 7.04(1H, d), 7.27(1H, d), 7.61(1H, s); \(^{13}\)C NMR \(\delta\) 7.7(CH\(_2\)), 12.2(CH), 20.6(CH\(_3\)), 124.3(CH, aromatic), 127.9(CH, aromatic), 133.3(CH, aromatic), 134.9(C, aromatic), 136.6(C, aromatic); \(\text{IR}\) \(\nu\) 1530(s), 1350(s); \(\text{MS(CI)}\) \(m/e\) 178(MH\(^+\), 37); MS(EI) 177(M\(^+\), 2.6), 149(37), 128(47), 115(93); \(\text{HRMS(CI)}\)

C\(_{10}\)H\(_{12}\)O\(_2\)N\(_1\), calc. 178.0868, exptl 178.0874 error 3.1 ppm.

7.4.2 Cyclopropynaphthalenes

1-Cyclopropynaphthalene. Into a 50 mL round-bottomed flask was added 33.6 mg (0.2 mmol) of 1-cyclopropynaphthalene and 10 mL CH\(_3\)CN/CH\(_3\)OH (9:1, v/v). 219.2 mg (0.4 mmol) of CAN was then introduced into flask which was fitted with stirrer, circulated with N\(_2\) and set in oil-bath. The reaction mixture was refluxed at a temperature of 55 °C for 10 hours and then poured into diethyl ether and water for workup. The combined ether layers was dried over anhydrous MgSO\(_4\), filtered and concentrated. First PTLC using 7:1 (v/v) hexane/EtOAc as solvents gave 7.4 mg (22%) of starting material 1-cyclopropynaphthalene, 18.3 mg (35%) 3-methoxy-3-naphthylpropynitrate and a mixture of 1-naphthylpropyl-1,3-dinitrate, 3-hydroxy-3-naphthylpropynitrate and 1- naphthyl-1,3-dimethoxypropane. Second PTLC with CHCl\(_3\) as solvent yielded 9.4 mg (20.4%) of 1-naphthyl-1,3-dimethoxypropane, 2.75 mg (4.7%) 1-naphthylpropyl-1,3-dinitrate and 2.15 mg (4.4%) of 3-hydroxy-3-naphthylpropynitrate. It was noted that 3-hydroxy-3-naphthylpropynitrate was produced in PTLC from 1-naphthylpropyl-1,3-dinitrate.
3-Methoxy-3-(1-naphthyl)propynitrate  $^1$H NMR $\delta$ 2.27(2H, m), 3.31(3H, s), 4.55(1H, m), 4.74(1H, m), 5.04(1H, t), 7.53(3H, m), 7.82(1H, d), 7.91(1H, d), 8.13(1H, d); $^{13}$C NMR $\delta$ 34.7(CH$_2$), 57.0(CH$_3$O), 70.4(CH$_2$), 77.7(CH), 122.8(CH, aromatic), 123.9(CH, aromatic), 125.4(CH, aromatic), 125.7(CH, aromatic), 126.3(CH, aromatic), 128.4(CH, aromatic), 129.1(CH, aromatic), 130.8(C, aromatic), 134.0(C, aromatic), 136.1(C, aromatic); IR $\nu$ 1633(s, O-N asymmetric stretching), 1281(s, O-N symmetric stretching), 1113, 862(p bond N-O linkage); MS(EI) m/e 262(M$^+$, 1.3), 261(M$^+$, 11), 171(M-CH$_2$CH$_2$ONO$_2$, 100), 153(54), 127(29); HRMS(EI) C$_{14}$H$_{15}$O$_4$N, expt'l 261.0994, calc. 261.1001, error -2.5 ppm.

1-Naphthylpropyl-1,3-dinitrate  $^1$H NMR $\delta$ 2.48(2H, m), 4.48(1H, m), 4.66(1H, m), 6.71(1H, t), 7.56(3H, m), 7.9(2H, m), 8.06(1H, d); $^{13}$C NMR $\delta$ 31.9(CH$_2$), 68.6(CH$_2$), 78.4(CH), 121.9(CH, aromatic), 123.5(CH, aromatic), 125.4(CH, aromatic), 126.3(CH, aromatic), 127.2(CH, aromatic), 129.3(CH, aromatic), 129.8(C, aromatic), 129.9(CH, aromatic), 132.6(C, aromatic), 133.7(C, aromatic); IR(CHCl$_3$) $\nu$ 3021, 1647(s), 1281, 1215(s); MS(EI) m/e 292(15.7), 127(100); HRMS(EI) C$_{13}$H$_{12}$O$_6$N$_2$, calc. 292.0695, expt'l 292.0688, error -2.5 ppm.

3-Hydroxy-3-(1-naphthyl)propynitrate  $^1$H NMR $\delta$ 2.07(1H, d, OH), 2.31(2H, m), 4.62(1H, m), 4.81(1H, m), 5.66(1H, m), 7.53(3H, m), 7.68(1H, d), 7.82(1H, d), 7.91(1H,d), 8.06(1H, d); $^{13}$C NMR $\delta$ 35.1(CH$_2$), 67.6(CH), 70.5(CH$_2$), 122.6(CH, aromatic), 122.7(CH, aromatic), 125.4(CH, aromatic), 125.8(CH, aromatic), 126.5(CH, aromatic), 128.6(CH, aromatic), 129.1(CH, aromatic), 129.9(C, aromatic), 133.8(C, aromatic), 139.0(C, aromatic); IR(CHCl$_3$) $\nu$ 3601(-OH), 3018, 1633, 1281, 1216(s);
MS(EI) m/e 248(M+1, 2.6), 247(M, 26), 230(M-OH, 6.5), 157(M-CH₂CH₂ONO₂, 88), 129(100); HRMS(EI) C₁₃H₁₃O₄N, calc. 247.0845, expt’l 247.083969, error -2.0 ppm.

1-Bromo-4-cyclopropynaphthalene. Into 50 mL round-bottomed flask was added 49.2 mg (0.2 mmol) of 1-Bromo-4-cyclopropynaphthalene and 10 mL CH₃CN/CH₃OH (9:1, v/v). 219.2 mg (0.4 mmol) of CAN was then introduced into flask which was fitted with stirrer, circulated with N₂ and set in oil-bath. The reaction mixture was refluxed at a temperature of 55 °C for 9 hours and then poured into diethyl ether and water for workup. The combined ether layers was dried over anhydrous MgSO₄, filtered and concentrated. First PTLC using 7:1 (v/v) hexane/EtOAc as solvents gave 12.4 mg (25.2%) of starting material 1-bromo-4-cyclopropynaphthalene, 22.6 mg (33.3%) 3-methoxy-3-(4-bromo-1-naphthyl)propynitrate and a mixture of 1-(4-bromo-1-naphthyl)propyl-1,3-dinitrate and 1-(4-bromo-1-naphthyl)-1,3-dimethoxypropane. Second PTLC with CHCl₃ as solvent yielded 8.64 mg (14%) of 1-(4-bromo-1-naphthyl)-1,3-dimethoxypropane and 11.66 mg (15.6%) 1-(4-bromo-1-naphthyl)propyl-1,3-dinitrate.

3-Methoxy-3-(4-Bromo-1-naphthyl)propynitrate ¹H NMR δ 2.24(2H, m), 3.30(3H, s), 4.56(1H, m), 4.74(1H, m), 5.01(1H, t), 7.41(1H, d), 7.60(2H, m), 7.81(1H, d), 8.11(1H, d), 8.34(1H, d); ¹³C NMR δ 34.8(CH₂), 57.1(CH₃O), 70.2(CH₂), 77.3(CH), 123.05(CH, aromatic), 123.1(C, aromatic), 124.3(CH, aromatic), 127.16(CH, aromatic), 127.18(CH, aromatic), 128.3(CH, aromatic), 129.7(CH, aromatic), 131.97(C, aromatic), 132.2(C, aromatic), 136.4(C, aromatic); IR(CHCl₃) ν 3018, 1632(s, O-N asymmetric stretching), 1280(s, O-N symmetric stretching), 1116(s), 1112, 866(p bond N-O linkage); MS(EI) m/e 341(M+2, 9.0), 339(M⁺, 8.6), 251(M+2-CH₂CH₂ONO₂, 100),
Chapter 7. Experimental

249(M-90, 97), 156(45), 152(69); **HRMS**(EI) C_{14}H_{14}O_{2}NBr, expt’l 339.0114, calc. 339.0106, error 2.2 ppm.

**1-(4-Bromo-naphthyl)propyl-1,3-dinitrate**  
1H NMR δ 2.45(2H, m), 4.49(1H, m), 4.67(1H, m), 6.67(1H, t), 7.44(1H, d), 7.67(2H, m), 7.82(1H, d), 8.06(1H, m), 8.37(1H, m); 13C NMR δ 31.9(CH$_2$), 68.4(CH$_2$), 77.8(CH), 122.2(CH, aromatic), 123.7(CH, aromatic), 124.8(C, aromatic), 127.8(CH, aromatic), 128.1(CH, aromatic), 128.6(CH, aromatic), 129.6(CH, aromatic), 130.9(C, aromatic), 132.2(C, aromatic), 132.9(C, aromatic); **IR**(CHCl$_3$) ν 3018, 1645(s), 1279, 1215(s), 850; **MS**(EI) m/e 372(M+2, 3.6), 370(M$^+$, 3.3), 280(M-90, 7.8), 278(M+2-90, 7.5), 233(32), 152(100); **HRMS**(EI) C$_{13}$H$_{11}$O$_6$N$_2$Br, calc. 369.9800, expt’l 369.9807, error 1.8 ppm.

**2-Cyclopropynaphthalene.** Into a 50mL round-bottomed flask was added 33.6 mg (0.2 mmol) of 2-cyclopropynaphthalene and 10 mL CH$_3$CN/CH$_3$OH (9:1, v/v). 219.2 mg (0.4 mmol) of CAN was then introduced into flask which was fitted with stirrer, circulated with N$_2$ and set in oil-bath. The reaction mixture was refluxed at a temperature of 55 °C for 11 hours and then poured into diethyl ether and water for workup. The combined ether layers was dried over anhydrous MgSO$_4$, filtered and concentrated. First PTLC using 3:1 (v/v) hexane/EtOAc as solvents gave 3.9 mg (11.6%) of starting material 2-cyclopropynaphthalene, 11.7 mg (22.4%) of 3-methoxy-3-(2-naphthyl)propynitrate, 8.56 mg (18.6%) of 1-(2-naphthyl)-1,3-dimethoxypropane and a mixture of 1-(2-naphthyl)propyl-1,3-dinitrate and 3-hydroxy-3-(2-naphthyl). Second PTLC with CHCl$_3$ as solvent yielded 9.58 mg (16.4%) of 1-(2-naphthyl)propyl-1,3-dinitrate and 8.45 mg
(17.1%) of 3-hydroxy-3-(2-naphthyl)propylnitrate. It was noted that 3-hydroxy-3-(2-naphthyl)propylnitrate was produced in PTLC from 1-(2-naphthyl)propyl-1,3-dinitrate.

**3-Methoxy-3-(2-naphthyl)propylnitrate**  
$^1$H NMR $\delta$ 2.10(1H, m), 2.26(1H, m), 3.27(3H, s), 4.43(1H, m), 4.52(1H, m), 4.66(1H, m), 7.44(1H, d), 7.50(2H, m), 7.75(1H, s), 7.85(3H, d); $^{13}$C NMR $\delta$ 35.3(CH$_2$), 56.8(CH$_3$O), 70.2(CH$_2$), 79.9(CH), 123.8(CH, aromatic), 125.9(CH, aromatic), 126.1(CH, aromatic), 126.4(CH, aromatic), 127.7(CH, aromatic), 127.8(CH, aromatic), 128.8(CH, aromatic), 133.2(C, aromatic), 138.1(C, aromatic), 139.5(C, aromatic); IR(CHCl$_3$) $\nu$ 3018, 1633(s), 1281, 1216(s); MS(EI) m/e 261(M$^+$, 13.6), 171(M-90, 100); HRMS(EI) C$_{14}$H$_{15}$O$_4$N, calc. 261.1001, expt’l 261.0999, error -0.9 ppm.

**1-(2-Naphthyl)propyl-1,3-dinitrate**  
$^1$H NMR $\delta$ 2.34(1H, m), 2.53(1H, m), 4.47(1H, m), 4.62(1H, m), 6.07(1H, t), 7.47(1H, d), 7.54(2H, m), 7.86(3H, m), 7.91(1H, d); $^{13}$C NMR $\delta$ 31.9(CH$_2$), 68.4(CH$_2$), 81.4(CH), 123.1(CH, aromatic), 126.3(CH, aromatic), 126.9(CH, aromatic), 127.0(CH, aromatic), 127.8(CH, aromatic), 128.1(CH, aromatic), 129.3(CH, aromatic), 128.3(C, aromatic), 133(C, aromatic), 133.6(C, aromatic); IR(CHCl$_3$) $\nu$ 3018, 1642, 1281, 1216(s); MS(EI) m/e 292(M$^+$, 10.7), 127(100); HRMS(EI) C$_{13}$H$_{12}$O$_6$N$_2$, calc. 292.0695, expt’l 292.0695, error -0.0 ppm.

**3-Hydroxy-3-(2-naphthyl)propylnitrate**  
$^1$H NMR $\delta$ 2.09(1H, d, OH), 2.33(2H, m), 4.57(1H, m), 4.71(1H, m), 5.02(1H, m), 7.82(4H, m); $^{13}$C NMR $\delta$ 35.8(CH$_2$), 70.2(CH$_2$), 72.9(CH), 123.4(CH, aromatic), 124.5(CH, aromatic), 126.2(CH, aromatic), 126.5(CH, aromatic), 127.7(CH, aromatic), 127.9(CH, aromatic), 128.8(CH, aromatic), 133.1(C, aromatic), 133.2(C, aromatic), 140.6(C, aromatic); IR(CHCl$_3$) $\nu$ 3605(-OH), 3018, 1636, 1281, 1215(s); MS(EI) m/e 248(M+1, 1.4), 247(M, 10), 246(M, 1).
Chapter 7. Experimental

230(M-OH, 6.5), 157(M-CH₂CH₂ONO₂, 30), 127(100); **HRMS**(El) C₁₃H₁₃O₄N, calc. 247.0845, exptl 247.0837, error -3.0 ppm.

7.4.3 Cyclopropylantracenes

**9-Cyclopropylantracene.** 26.6 mg (0.122 mmol) of 9-Cyclopropylantracene was dissolved in 10 mL CH₃CN/CH₃OH (9:1, v/v) and 267.4 mg (0.488 mmol) CAN (mole ratio of CAN to 9-cyclopropylantracene = 4) was than added. The reaction proceeded immediately. The orange color of the Ce(IV) solution disappeared and instead, a white solid (Ce(III) salt) in the solution was observed. The reaction mixture was stirred under nitrogen at room temperature for 20 minutes and then poured into water and extracted with diethyl ether. The ether layers was dried over anhydrous MgSO₄, filtered and concentrated. Products was separated by preparative thin layer chromatography CH₂Cl₂ as solvent, which yielded 6.5 mg (22%) of 9-cyclopropyl-10-methoxyanthracene, 15.4 mg (48%) of 9-cyclopropyl-9-methoxyanthrone. 21% of anthraquinone and 2% of 9-cyclopropyl-9-methoxy-10,10-dimethoxyanthracene were also obtained based on GC analysis.

Another run began with 49.05 mg (0.225 mmol) of 9-cyclopropylantracene and 274 mg (0.50 mmol) of CAN. The reaction proceeded under same condition and the resulting solution was worked up with H₂O/diethyl ether. PTLC with 3:1 hexane/CH₂Cl₂ as solvents yielded 16.2 mg (29%) of 9-cyclopropyl-10-methoxyanthracene and 5.5 mg (10%) of starting material and a mixture of anthraquinone, 9-cyclopropyl-9-methoxyanthrone and 9-cyclopropyl-9-methoxy-10,10-dimethoxyanthracene. Second PTLC of the mixture with 5:1 hexane/EtOAc as solvent yielded 5.7 mg (9%) of 9-
cyclopropyl-9-methoxy-10,10-dimethoxyxanthracene, 11.9 mg (17%) of 9-cyclopropyl-9-methoxyanthrone and 4.0 mg (9%) of anthraquinone (Table 5-1).

Product distribution of CAN oxidation of 9-cyclopropylanthracene in four different mole ratios of CAN to 9-cyclopropylanthracene were examined in the following experiment: Into each of four small vials was placed 5.6 mg (0.0257 mmol) and 1 mL CH$_3$CN/CH$_3$OH (9:1, v/v). 13.7 mg (0.025 mmol), 27.4 mg (0.050 mmol), 41.4 mg (0.075 mmol) and 54.8 mg (0.10 mmol) of CAN were added to four vials, respectively. After 20 minutes, the reaction mixtures were worked up with H$_2$O/diethyl ether, dried over MgSO$_4$, filtered and evaporated to dryness. 5 mL CH$_3$CN was added into each of vials to dissolve the residue. 0.04 mL of the solution was taken and diluted into 2 mL with CH$_3$CN. HPLC was employed to analyze amount of products in each of four samples. The standard solutions of starting material 9-cyclopropylanthracene (0.01 mg/mL) and major product 9-cyclopropyl-10-methoxyanthracene (0.01 mg/mL) and 9-cyclopropyl-9-methoxyanthrone (0.04 mg/mL) in CH$_3$CH were prepared and HPLC correction factors for these compounds [1.0 × 10$^{-4}$ (mg/mL)/area, 1.44 × 10$^{-4}$ (mg/mL)/area and 1.41 × 10$^{-4}$ (mg/mL)/area, respectively] were determined. The HPLC yields of products thus obtained were summarized in Table 5-2 (HPLC condition: CH$_3$CN/H$_2$O = 9:1, flow rate = 1 mL/min, UV detector: λ= 256 nm).

**9-Bromo-10-cyclopropylanthracene.** The reaction of 9-bromo-10-cyclopropylanthracene with CAN was performed in a similar procedure as that for 9-cyclopropylanthracene. One run of reaction began with 42.2 mg (0.143 mmol) of 9-bromo-10-cyclopropylanthracene and 164.4 mg (0.30 mmol) of CAN. The reaction was
run in 10 mL 9:1(v/v) CH$_3$CN/CH$_3$OH for 20 min. The resulting solution was worked up and the products were isolated by PTLC with 3:1 hexane/CH$_2$Cl$_2$ as solvents, which gave 30.8 mg (60%) of 9-cyclopropyl-9-methoxyanthrone. 9% of anthraquinone was also obtained based on GC analysis.

Another run of reaction was performed in a 1 mL 9:1 (v/v) CH$_3$CN/CH$_3$OH containing 6.3mg (0.021mmol) of 9-bromo-10-cyclopropylantracene and 24.7 mg (0.045 mmol) of CAN. The yield of product was determined by HPLC (HPLC condition: CH$_3$CN/H$_2$O = 9:1, flow rate = 1 mL/min, UV detector: $\lambda$= 256 nm ). The standard curve method gave 4.3 mg (76.5%) of 9-cyclopropy-9-methoxyanthrone (0.01 mg/mL standard solution of 9-cyclopropy-9-methoxyanthrone). 8% of anthraquinone was also obtained based on GC analysis (Table 5-3).

7.4.4 9, 10-Dialkylanthracenes

**9,10-Dimethylanthracne (DMA)**

**Run 1.** 20 mg (0.097 mmol) of DMA was introduced into a 3-dram-vial and then 5 mL of CH$_3$CN/CH$_3$OH (9:1, v/v) was added. The solution (pale yellow) was stirred and kept in ice-bath (0 °C) for 5 min (DMA does not dissolve well in CH$_3$CN/CH$_3$OH). 101 mg (0.184 mmol, 1.9 equiv.of DMA) of CAN was added slowly and blue color of solution was noted at moment of CAN addition. The reaction mixture was stirred at 0 °C for 30 min and the resulting solution was colorless. The reaction mixture was poured into 20 mL diethyl ether and then water was added to do extraction. The ether layer was separated from water, dried over anhydrous MgSO$_4$, and filtered. White solid was obtained after concentrated. 0.6 mL CDCl$_3$ was added to rinse the solid
and CDCl₃ solution was then transferred into NMR tube. After 2 µL [(CH₃)₃Si]₂O (internal standard) was introduced, ¹H NMR was run to determine the yields of products, according to

\[ W_X = 0.1527 \left( \frac{M_X V_S}{N_X} \right) \left( \frac{A_X}{A_S} \right) \]

where, \( W_X \) is weight of product \( X \) (mg), \( M_X \) molecular weight of \( X \), \( V_S \) volume of internal standard \( S \) (µL), \( N_X \) number of protons integrated for product \( X \), \( A_X \) area of integration for product \( X \), and \( A_S \) area of integration for internal standard \( S \). ¹H NMR showed that 9,10-dimethoxy-9,10-dimethylanthracene is only major product with a yield of 25.55 mg (98.3%). No trace of 9-methoxymethyl-10-methylanthracene was detected by ¹H NMR. PTLC was employed to isolate the product 9,10-dimethoxy-9,10-dimethylanthracene from reaction mixture and CHCl₃ was used as solvent.

**9,10-Dimethoxy-9,10-dimethylanthracene** ¹H NMR δ 1.63(s, 6H, methyl), 2.79(s, 6H, methoxy), 7.41(m, 4H, aromatic), 7.68(m, 4H, aromatic); ¹³C NMR δ 35.9(methyl), 51.5(methoxy), 75.1(q-C), 126.0(CH, aromatic), 127.9(CH, aromatic), 138.6(C, aromatic); IR(CHCl₃) ν 1446, 1371, 1268, 1215(s), 1090, 1035; MS(CI) m/e 269(MH⁺, 1.75), 253(M-15), 237(MH⁺-32, 100), 205(MH⁺-64, 35); MS(EI) m/e 268(M⁺, trace), 253(M-15, 36), 237(M-31, 38), 222(M-46, 52), 207(M-61, 100), 206(M-62, 72).

**Run 2.** The experimental procedure is the same as that in run 1 except that reaction was controlled at 45 °C for 30 min. The reaction yielded 9.34 mg (40.8%) of 9-methoxymethyl-10-methylanthracene and 13.79 mg (53%) of 9,10-dimethoxy-9,10-dimethylanthracene. PTLC with CHCl₃ as solvent gave the pure 9-methoxymethyl-10-methylanthracene.
9-Methoxymethyl-10-methylanthracene \[ ^1H \text{NMR} \delta \; 3.13 (s, 3\text{H, methyl}), 3.55 (s, 3\text{H, methoxy}), 5.44 (s, 2\text{H, methylene}), 7.53 (m, 4\text{H, aromatic}), 8.34 (m, 2\text{H, aromatic}), 8.42 (m, 2\text{H, aromatic}); \]
\[ ^{13}\text{C NMR} \delta \; 35.9 (\text{methyl}), 58.3 (\text{methoxy}), 66.8 (\text{methylene}), 124.8 (\text{CH, aromatic}), 124.9 (\text{CH, aromatic}), 125.3 (\text{CH, aromatic}), 125.6 (\text{CH, aromatic}), 129.8 (\text{C, aromatic}), 130.7 (\text{C, aromatic}), 131.9 (\text{C, aromatic}), 138.6 (\text{C, aromatic}); \]
\[ \text{IR (CHCl}_3) \nu \; 1463, 1279, 1214 (s), 1092; \text{MS (EI)} \; m/e \; 237 (M^+, 9.5), 236 (M^+, 48), 221 (M-15, 13), 205 (M-31, 100); \text{HRMS (EI)} \text{ for C}_{17}\text{H}_{16}\text{O, calc. 236.1201, expt'l 236.1210, error 3.8 ppm.} \]

The NMR tube containing pure 9-methoxymethyl-10-methylanthracene in CDCl\textsubscript{3} was placed in refrigerator. After several days some amount 9-methoxymethyl-10-methylanthracene was found converted to 9-methoxy-9-methyl-10-methyleneanthracene. PTLC with CHCl\textsubscript{3} as solvent gave the pure product.

9-Methoxy-9-methyl-10-methyleneanthracene \[ ^1H \text{NMR} \delta \; 2.14 (s, 3\text{H, CH}_3), 3.66 (s, 3\text{H, OCH}_3), 4.54 (s, 2\text{H, =CH}_2), 7.27 (m, 4\text{H, aromatic}), 7.38 (m, 2\text{H, aromatic}), 7.46 (m, 2\text{H, aromatic}); \]
\[ ^{13}\text{C NMR} \delta \; 13.6 (\text{methyl}), 60.2 (\text{methoxy}), 69.6 (\text{methylene}), 119.9 (\text{q-C}), 120.7 (\text{CH, aromatic}), 121.8 (\text{CH, aromatic}), 127.3 (\text{CH, aromatic}), 127.4 (\text{CH, aromatic}), 130.7 (\text{q-C, methylene}), 138.9 (\text{C, aromatic}), 140.9 (\text{C, aromatic}); \]
\[ \text{IR (CHCl}_3) \nu \; 1463, 1223 (s), 1122; \text{MS (EI)} \; m/e \; 237 (M^+, 9.5), 236 (M^+, 48), 221 (M-15, 13), 205 (M-31, 100); \text{HRMS (EI)} \text{ for C}_{17}\text{H}_{16}\text{O, calc. 236.1201, expt'l 236.1197, error -1.6 ppm.} \]

Run 3. 40 mg (0.194 mmol) of DMA and 202 mg (0.368 mmol, 1.9 equiv. of DMA) of CAN reacted in 9:1 (v/v) CH\textsubscript{3}CN/CH\textsubscript{3}OH at 0 °C for 30 min (follow the procedure in run 1). The reaction mixture was equally divided into two portions. One
portion was directly worked up and products was analyzed by $^1$H NMR, which exclusively yielded 24.54 mg (94.3%) of 9,10-dimethoxy-9,10-dimethylandanthracene. Another portion was heated at 45°C for 30 min and was then worked up. The $^1$H NMR analysis gave 9.85 mg (43.0%) of 9-methoxymethyl-10-methylanthracene and 12.75 mg (49.0%) of 9,10-dimethoxy-9,10-dimethylandanthracene.

**Run 4.** The experimental procedure is the same as that in run 1 except that reaction was run in pure CD$_3$CN (no methanol) at 0 °C for 30 min. The reaction mixture was filtered through cotton to NMR tube and was subject to run $^1$H NMR. $^1$H NMR showed that there was no signal related to deprotonation product. The work up of this CD$_3$CN solution with water/ether gave deprotonation product. PTLC with CHCl$_3$ as solvent gave 9-(10-methylanthryl)methyl nitrate: $^1$H NMR $\delta$ 3.18(s, 3H, methyl), 6.54(s, 2H, methylene), 7.62(m, 4H, aromatic), 8.36(m, 4H, aromatic).

**9-Cyclopropyl-10-methylanthracene (MCPA)**

**Run 1.** 20 mg (0.0862 mmol) of MCPA and 89.8 mg (0.0.164 mmol, 1.9 equiv. of MCPA) of CAN reacted in 9:1 (v/v) CH$_3$CN/CH$_3$OH at 0 °C for 30 min (following the procedure in run 1 of CAN oxidation of DMA in CH$_3$CN/CH$_3$OH). After work-up, 22.85 mg (90.5%) of 9-cyclopropyl-9,10-dimethoxy-10-methylanthracene was obtained as only major product, based on $^1$H NMR analysis. PTLC with CHCl$_3$ as solvent gave pure product.

**9-Cyclopropyl-9,10-dimethoxy-10-methylanthracene** $^1$H NMR $\delta$ 0.35(m, 2H, cis-CP-methylene), 0.54(m, 2H, trans-CP-methylene), 1.14(m, 1H, methine), 1.71(s, 3H, methyl), 2.72(s, 3H, methoxy), 2.82(s, 3H, methoxy), 7.41(m, 4H, aromatic), 7.63(m,
Chapter 7. Experimental

2H, aromatic), 7.70(m, 2H, aromatic); $^{13}$C NMR $\delta$ 2.20(CP-methylene), 27.0(CP-methylene), 35.8(methyl), 51.3(methoxy), 75.1(q-C), 76.3(q-C), 126.2(CH, aromatic), 126.5(CH, aromatic), 127.4(CH, aromatic), 127.9(CH, aromatic), 137.5(C, aromatic), 140.0(C, aromatic); IR(CHCl$_3$) $\nu$ 1476, 1446, 1216(s), 1087, 1062; MS(Cl) m/e 295(MH$^+$, 3.5), 263(MH$^+-32$, 100); MS(EI) m/e 294(M$^+$, 0.75), 279(M-15, 6.5), 266(34), 253(31), 233(16), 222(54), 207(54), 192(100).

Run 2. The experimental procedure is the same as that in run 1 except that reaction was controlled at 45 °C for 30 min. The reaction yielded 8.42 mg (37.3%) of 9-cyclopropyl-10-methoxymethylanthracene and 14.55 mg (57.4%) of 9-cyclopropyl-9,10-dimethoxy-10-methylanthracene. PTLC with CHCl$_3$ as solvent gave pure 9-cyclopropyl-10-methoxymethylanthracene.

9-Cyclopropyl-10-methoxymethylanthracene $^1$H NMR $\delta$ 0.77(m, 2H, cis-CP-methylene), 1.46(m, 2H, trans-CP-methylene), 2.51(m, 1H, CP-methylene), 3.56(s, 3H, methoxy), 5.42(s, 2H, methylene), 7.52(m, 4H, aromatic), 8.39(m, 2H, aromatic), 8.81(m, 2H, aromatic); $^{13}$C NMR $\delta$ 9.70(CP-methylene), 10.9(CP-methylene), 58.4(methoxy), 66.7(methylene), 124.5(CH, aromatic), 124.6(CH, aromatic), 125.6(CH, aromatic), 126.5(CH, aromatic), 128.1(C, aromatic), 130.7(C, aromatic), 131.4(C, aromatic), 136.6(C, aromatic); IR(CHCl$_3$) $\nu$ 1663, 1601, 1447, 1317, 1279, 1215(s), 1091; MS(EI) m/e 263(M+1, 5), 262(M$^+$, 29), 231(M-31, 22), 230(35), 215(100); HRMS(EI) for C$_{19}$H$_{18}$O, calc. 262.1358, expt’l 262.1351, error -2.5 ppm.

The NMR tube containing pure 9-cyclopropyl-10-methoxymethylanthracene in CDCl$_3$ was placed in refrigerator. After several days some amount of 9-cyclopropyl-10-
methoxymethylandanthracene was found converted to 9-cyclopropyl-9-methoxy-10-methyleneanthracene. PTLC with CHCl₃ as solvent gave the pure product.

**9-Cyclopropyl-9-methoxy-10-methyleneanthracene**  IR(CHCl₃) ν 1553, 1419, 1215(s); MS(EI) m/e 263(M⁺, 13), 262(M⁺, 45), 231(M-31, 39), 230(52), 215(100); HRMS(EI) for C₁₉H₁₈O, calc. 262.1358, expt’l 262.1359, error 0.6ppm.

**Control Experiment.** 20 mg (0.0746 mmol) of 9,10-dimethoxy-9,10-dimethylandanthracene in 0.9 mL CDCl₃ (colorless) was heated at 50°C for one hour. ¹H NMR showed that no reaction occurred. 2 drops of H₃PO₄ (98%) and 0.1 mL of CH₃OH were then added and heated at 50 °C for about 15min. The solution color changed into yellow. After work-up with diethyl ether and water. ¹H NMR was run to determine the yield of products. 57% of 9,10-dimethoxy-9,10-dimethylandanthracene was converted into 9-methoxymethyl-10-methylandanthracene and the yield was about 100%.
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222


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(91) \( \frac{\partial \log(v_c)}{\partial \log[2]} = 1 \) is consistent with two rate laws: \( k[2^+]^2 \) or \( k[2][2^+] \). However, only the former is consistent with the LSV results.

(92) Simulations were performed using DigiSim 2.1 (R) - A General Simulation Program for Cyclic Voltammetry, Rudolph M.; Feldberg, S., Distributed by Bioanalytical Systems Inc., 2701 Kent Ave, West Lafayette 47906 USA.


(96) This kinetic analysis is based upon \( k_{\text{dim}} \) for \( 2^+ \). It is expected that \( k_{\text{MeOH}} \) for \( 1^+ \) is even slower. Dinnocenzo has shown that for substituted cyclopropylbenzene radical cations, the rate of nucleophile-induced ring opening correlates to \( \sigma^+ \) (and is facilitated by electron withdrawing groups). For Br, \( \sigma^+ = 0.15 \), vs. 0.0 for H.

(97) RSE’s for \( \text{ArCH}_2 \cdot \) were taken as the difference in the bond strength of \( \text{ArCH}_2\text{H} \) (88.0, 85.1, and 85.7 kcal/mol for \( \text{Ar} = \text{C}_6\text{H}_5, \alpha-, \text{and} \beta-\text{C}_{10}\text{H}_7 \), respectively) and \( \text{CH}_3\text{CH}_2\text{H} \) (98.2 kcal/mol). Bond strengths were taken from McMillen, D.; Golden,
D., *Ann. Rev. Phys. Chem.*, **1982**, 33, 493. The BDE of $\beta$-C$_{10}$H$_7$CH$_2$-H was not available and was estimated using $\Delta H_f^{\infty}$s obtained using SCF-MO theory (AM1).


(103) Wang, Y.; Tanko, J., Unpublished results at Virginia Polytechnic Institute and State University.


(121) Simulations were performed using DigiSim 2.0, (Bioanalytical Systems, Inc., W. Lafayette, IN) for the rate laws $k_{\text{obs}}[A][B]$ and $k_{\text{obs}}[B]^2$, where $k_{\text{obs}} = k$ [CH$_3$OH]. For the data in Figure 4-12→4-15, the cathodic current ($I_{\text{pc}}$) is measured from the
zero-current axis. The pseudo second order rate constant $k_{obs}$ was found to vary with [CH$_3$OH]: $k_{obs} = 4.3 \times 10^3$, $1.1 \times 10^4$, and $2.6 \times 10^4$ M$^{-1}$s$^{-1}$ at 0.25, 0.5, and 1.0 M CH$_3$OH, respectively. Thus, based upon CV analysis, the overall rate law is $k[A][B][X]$ with $k = 2.9 \times 10^4$ M$^{-2}$s$^{-1}$.


(123) The factors which affect whether radical cation decay might occur via disproportionation have been extensively discussed by Parker, see reference (112).


(125) As might be expected, the electron-donating methoxy in 7 causes the molecule to be more easily oxidized than starting compound 1. The CV of 7 exhibits a peak potential of +676 mV (0.69 mM in CH$_3$CN/LiClO$_4$). Under analogous conditions, $E_P$ for 1 is ca. 750 mV.


(131) Spin densities for the H(1s) orbital were determined using the keywords UHF and ESR, and converted to hyperfine coupling constants using the relationship: $a_H =$
The constant 382 G is derived from the experimentally observed $\alpha_H^1$ for the methyl radical (23.0 G) and the AM1-calculated spin density in H(1s) (0.0602). Hyperfine coupling constants calculated in this manner nicely duplicate experimental values for several cyclopropane-containing radicals and radical ions. For example, the observed hyperfine couplings for the cyclopropylcarbinyl radical (which adopts the bisected conformation) are $\alpha_H^\alpha = 20.74$ G, $\alpha_H^\beta = 2.55$ G, $\alpha_H^\chi = 2.01, 2.98$ G (Kochi, J.; Krusic, P.; Eaton, D., J. Am. Chem. Soc., 1969, 91, 1877). The AM1-derived values are $\alpha_H^\alpha = 21.8$ G, $\alpha_H^\beta = 2.65$ G, $\alpha_H^\chi = 0.68, 1.6$ G. For 9-cyclopropylanthracene radical anion (which adopts the perpendicular conformation), AM1 predicts $\alpha_H^\beta = 5.9$ G (experimentally, $\alpha_H^\beta = 6.64$ G; reference 23).

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In the Fall of 1979 he enrolled at Henan Normal University, Xinxiang, China with a dream of becoming a chemistry teacher. After receiving a Bachelor of Science in chemistry in 1983, he was admitted to the graduate school at Northeast University, Shenyang, China. He studied analytical chemistry under the guidance of Prof. Shousong Zhang and quickly obtained his Master’s degree in 1985.

In December of 1985 he became a faculty member of the Department of Environmental Engineering at Xian University of Architecture and Technology, Xian, China. He was promoted to Lecturer in 1988, vice-director of Environmental Engineering Division and associate professor in 1993.

In the fall of 1993 he entered the doctoral program at Virginia Polytechnic Institute and State University where he worked in the area of organic chemistry under the guidance of Prof. James M. Tanko. He received a Doctor of Philosophy in chemistry in June, 1997.

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