Reductive Photocarboxylation of Aromatic Hydrocarbons in Supercritical CO2: A Mechanistic Investigation

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REDUCTIVE PHOTOCARBOXYLATION OF AROMATIC HYDROCARBONS IN SUPERCRITICAL CO₂: A MECHANISTIC INVESTIGATION

by
Jingsheng Zhang

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the requirements for the Degree of Master of Arts
Department of Chemistry

Western Michigan University
Kalamazoo, Michigan
December 2000
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Jingsheng Zhang
2000
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Jingsheng Zhang
REDUCTIVE PHOTOCARBOXYLATION OF AROMATIC HYDROCARBONS
IN SUPERCRITICAL CO\textsubscript{2}: A MECHANISTIC
INVESTIGATION

Jingsheng Zhang, M.A.
Western Michigan University, 2000

Recent research interest on supercritical CO\textsubscript{2} includes the following three important issues: 1) the development of supercritical CO\textsubscript{2} as an environmental benign reaction medium and as a viable alternative to hazardous organic solvents, 2) the use of supercritical CO\textsubscript{2} as a C\textsubscript{1} feedstock for fixation of CO\textsubscript{2} and 3) characterization of photoinduced electron transfer reactions under supercritical conditions.

The reductive photocarboxylation of aromatic hydrocarbons such as anthracene and phenanthrene in supercritical CO\textsubscript{2}, have been chosen for study. Supercritical CO\textsubscript{2} was utilized as both a replacement solvent and as a reacting reagent for the formation of carbon-carbon bonds and addition of a functional group. By comparison with similar reactions in regular organic solvents, photocarboxylation in supercritical CO\textsubscript{2} has higher yield and selectivity. This fundamental study helped to understand the influence of supercritical CO\textsubscript{2} as a solvent and its influence on photocarboxylation reactions. The mechanistic investigation combined with time-resolved laser flash photolysis and other spectroscopic methods, shows that carboanion radical intermediates are involved in this photoinduced electron transfer process.
# TABLE OF CONTENTS

ACKNOWLEDGMENTS .......................................................................................................................... ii

LIST OF TABLES ...................................................................................................................................... iv

LIST OF FIGURES ..................................................................................................................................... v

INTRODUCTION ....................................................................................................................................... 1

  Background Information .......................................................................................................................... 1
  CO₂ Fixation and Photoinduced Electron Transfer Reactions ................................................................... 1
    CO₂ Fixation ......................................................................................................................................... 1
    Photoinduced Electron Transfer (PET) .................................................................................................. 4

  Supercritical Fluids (SCF) ..................................................................................................................... 6
    Physical Properties of Supercritical Fluids ............................................................................................ 6
    Supercritical CO₂ (SC CO₂) .................................................................................................................. 7

Reaction Chemistry in Supercritical CO₂ and Applications ...................................................................... 10

Radical and Radical Ion in Supercritical Fluids .................................................................................... 12

EXPERIMENTAL SECTION ....................................................................................................................... 14

  Materials ............................................................................................................................................... 14

  Photoreactions and Apparatus ............................................................................................................... 14

    Photoirradiation of Aromatic Hydrocarbon-DMA-supercritical CO₂ System .................................... 14
    Photoirradiation for Aromatic Hydrocarbon-DMA-ACN (or DMF) System ..................................... 16

    Influence of Different Hydrogen Donor on Yield and Selectivity .................................................... 17

  Preparation of Chemicals ....................................................................................................................... 17

  .............................................................................................................................................................. iii
LIST OF TABLES

1. Bulk Properties of Supercritical Fluids ................................................................. 7
2. Condition Parameters for HPLC Product Analysis .................................................... 21
3. Photoreaction of Aromatic Hydrocarbons (ArH) With DMA, Cyclohexane in Supercritical \( \text{CO}_2 \) .................................................................................................................... 31
4. Solvent Effects on Photocarboxylation of Anthracene With DMA ....................... 32
5. Reactions at Various \( \text{CO}_2 \) Pressure at \( 35 \pm 0.2^\circ \text{C} \) ................................ 38
6. Effects of Various Hydrogen Donors ........................................................................ 39
## LIST OF FIGURES

1. Photocarboxylation Reactions Reported by Tazuke and Coworkers .................. 3
2. Photoinduced Electron Transfer Process .......................................................... 4
3. Generic Temperature – Pressure Phase Diagram of a Substance ..................... 8
4. Temperature – Pressure Phase Diagram of Pure CO₂ ...................................... 8
5. Density Tunability in Supercritical CO₂ ............................................................ 9
6. Stainless Steel High-Pressure Optical Cell ...................................................... 15
7. Block Picture of High-Pressure Photolysis Apparatus .................................... 16
8. Preparation of 9,10-Dihydro-9-anthracenecarboxylic Acid ......................... 18
9. H¹NMR Spectrum of 9,10-Dihydro-9-anthracenecarboxylic Acid ................ 20
10. Laser Flash Photolysis Apparatus ................................................................. 22
11. Electronic Energy Levels and Transitions ....................................................... 23
12. π → π* Transition ......................................................................................... 24
13. UV-vis Spectrum of Anthracene in Acetonitrile .......................................... 25
14. UV-vis Spectrum of Phenanthrene in Acetonitrile, [PHN] = 0.0005M ............. 26
15. UV-vis Absorption Spectrum of N,N-dimethylaniline in Acetonitrile .......... 27
16. UV-vis Spectra of Reaction Mixture, Pressure=1800psi, Temperature=35°C: (a) Before Photoirradiation; (b) After 2-Hour Photoirradiation at 366nm ......... 27
17. UV-vis Spectrum of 9,10-Dihydro-9-anthracenecarboxylic Acid ................. 28
18. HPLC Spectrum of Anthracene-DMA-2-Propanol Reaction Products Mixture ................................................................. 29
<table>
<thead>
<tr>
<th>Number</th>
<th>Figure Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>HPLC Spectrum of Anthracene-DMA-Cyclohexane Product Mixture by Gradient Elution</td>
<td>30</td>
</tr>
<tr>
<td>20</td>
<td>Anthracene Dimmer (Compound VIII)</td>
<td>32</td>
</tr>
<tr>
<td>21</td>
<td>The General Pathway and Intermediates in Bimolecular Photoinduced Electron Transfer Reactions in a Fluid Solvent</td>
<td>33</td>
</tr>
<tr>
<td>22</td>
<td>Solvent Separated Radical Ion Pairs and Contact Radical Ion Pair</td>
<td>34</td>
</tr>
<tr>
<td>23</td>
<td>The Microstructures of Solvent-solute Clustering With and Without Cosolvent</td>
<td>37</td>
</tr>
<tr>
<td>24</td>
<td>Proposed Reaction Paths for Photocarboxylation of Phenanthrene in Supercritical Carbon Dioxide</td>
<td>40</td>
</tr>
<tr>
<td>25</td>
<td>Steric Structure of DMA and its Possible Coupling Products With Aromatic Hydrocarbon Anion Radicals</td>
<td>41</td>
</tr>
<tr>
<td>26</td>
<td>Reasonable Structures for DMA Radical Cation</td>
<td>42</td>
</tr>
<tr>
<td>27</td>
<td>Transient Absorption Spectra of Phenanthrene With DMA in Acetonitrile With 355nm Laser Excitation</td>
<td>43</td>
</tr>
<tr>
<td>28</td>
<td>Transient Absorption Spectra of Pure Phenanthrene in Acetonitrile With 355nm Laser Excitation</td>
<td>44</td>
</tr>
<tr>
<td>29</td>
<td>Transient Absorption Spectrum of Anthracene With Triethylamine in Acetonitrile With 266nm Laser Excitation</td>
<td>44</td>
</tr>
<tr>
<td>30</td>
<td>Transient Absorption Spectra of Phenanthrene With DMA in Supercritical CO₂ With 355nm Laser Excitation</td>
<td>45</td>
</tr>
</tbody>
</table>
INTRODUCTION

Background Information

CO₂ Fixation and Photoinduced Electron Transfer Reactions

**CO₂ Fixation**

Since it can reductively convert atmospheric and chemically recovered carbon dioxide, CO₂ fixation has very important energy and environmental consequences.¹ In nature, CO₂ can be processed by biophotosynthesis to produce fossil fuels. In industrial and synthetic applications, fixation of CO₂ by using it as a C₁-building block in chemical synthesis has gained considerable interest, mainly spurred by its abundant availability and ecologic reasons.

The chemical fixation of CO₂ is motivated by two objectives: (a) To exploit a widely available raw material yielding valuable products, e.g. the electrocarboxylation of organic compounds using sacrificial Mg anodes. (b) To mitigate the increase in atmospheric CO₂, by processes with a favorable total CO₂ consumption budget, as a possible countermeasure against global warming caused by CO₂ emission.²

Currently CO₂ technology includes electronic discharging and catalytic reduction. Carbon dioxide utilization via gas discharges plasma chemical processing is reported, including the indirect and direct conversion of carbon dioxide to more valuable compounds with the discharge systems of H₂ + CO₂, CH₄ + CO₂, H₂O + CO₂, and H₂S + CO₂.³ However, the reduction potential of CO₂ to CO₂⁻ is reported to be −2.21V vs SCE in DMF.⁴ Since there is a large kinetic barrier to overcome the linear structure of carbon dioxide, the direct one electron reduction of CO₂ is
unfortunately energetically unfavorable.

A number of routes to reduce CO₂ by catalysts, such as metal oxides (MgO, CoO, and TiO₂ etc.), have been developed. Catalysis provides several opportunities to convert CO₂ to valuable chemicals, such as alcohols, amines, and formic acid derivatives. However, catalysts bring us alternative environmental concerns.

Carbon dioxide is one of most stable carbon compounds with a well-known linear molecular structure. The structure also has a large partial negative charge because of quadruple moment. So it is possible to process a nucleophilic attack by a carbon-centered nucleophile to form C-C coupling product. Tazuke and coworkers have reported the direct reduction of CO₂ by aromatic radical anions. The mechanism of reductive carboxylation of anthracene, phenanthrene and pyrene in polar nonprotic organic solvents, such as DMF, DMSO, CH₃CN, etc. has been investigated. The carboxylation products of aromatic hydrocarbons were reported under photoirradiation in presence of amines, usually N, N-dimethylaniline (DMA). Figure 1 presents reported products under 366nm irradiation of the aromatic hydrocarbons in DMF with DMA and 1 atmosphere (DMF saturated solution) of CO₂. Recent advances in photoinduced electron-transfer reactions make it instructive to consider the mechanism involved in such a photochemical reduction.

Another example was given by Wada and coworkers recently. They investigated the photofixation of carbon dioxide into benzophenone under visible light photoirradiation. In their study, triethylamine was used as an electron donor, and a certain photocatalyst was added to enhance the formation of radical anion, which was considered as the electron pool for the photofixation.
Figure 1. Photocarboxylation Reactions Reported by Tazuke and Coworkers.6
Photoinduced Electron Transfer (PET)

Photon energy absorbed by a chemical system may be used to transfer an electron between an electron donor (D) and an electron acceptor (A). Primarily a pair of high-energy intermediates (usually radical ions) is generated in specific solvation and spin states after light absorption. Then there are two pathways considered to finish the migration of an electron between donors and acceptors with photo energy: 1) the energy is deposited into the components of the electron transfer system, that is intramolecular excitation; 2) the ground state donors and acceptors form charge-transfer complexes, electron promotion involves such intermolecular transfer. The forward electron transfer process is often accompanied by the energy-wasting back-electron transfer (BET) within the pair of reactive intermediates. Since the high-energy intermediates dynamically keep changing, for example: the ions are solvated, the radical ions or radicals are separated by diffusion control, or spin status of radical pairs are changing. The BET step is a small degree in the process in most cases.

Forward electron transfer – PET, determines the energy usefulness of the overall process. In Figure 2, an excited singlet state $A^*$ acts as an electron acceptor when reacting with an electron donor (D). A pair of reactive intermediates is the result of forward ET. Depending on solvation, photoinduced electron transfer between donor and acceptor produces to either exciplex formation ($A\ldots D^*$) or ionic dissociation with more charge transfer character ($A^-\ldots D^+$). Then finally a free radical ion with charge-separated will form if the solvent is enough polar.

$$A^* + D \rightarrow (A\ldots D^*) \rightarrow (A^-\ldots D^+) \rightarrow A^- + D^+$$

Figure 2. Photoinduced Electron Transfer Process.
Recent progress in flash photolysis spectroscopy provides evidence for this mechanism by observing short-lived transients formed during a photochemical reaction. A pulse of light from a lamp or laser generates the intermediates, which can be spectroscopically detected by absorbance, fluorescence, resonance Raman, or conductivity. The lifetime of the flash photolysis pulse could be in range of millisecond long or femtosecond short. To detect the transient accurately, the lifetime of the transient should be longer than the width of flash photolysis pulse.

The most widely used and powerful method today is UV-Vis absorption for detection of transients in photochemical reaction. The detection systems are set up to measure the change of optical density vs. time at a fixed wavelength. Then a transient spectrum can be obtained by plotting intensity of the signal vs. monitored wavelength. The known spectra of cation radicals or anion radicals or excited-state absorption spectra are used as references for the transient spectra.

Many ion radicals generated by photoinduced electron transfer will fluoresce if excited by light after the initial pulse. For example, 9-xanthenyl cation has relatively intense fluorescence emission at 533nm with a long lifetime in trifluoroacetic acid and acetonitrile mixed solvent. The fluorescence spectra of the transient can be compared to known spectra.

One can measure the formation or decay of the transient signal as a function of time. Based on this, the kinetics of photoinduced electron transfer or the reactions, which make the disappearance of the transient species, can be studied. With ideal conditions, one can observe the decay spectra of the excited state involved in the photoinduced electron transfer reaction along with increase in both the cation and anion radical. Also one may be able to obtain the decay of each species individually. This procedure can produce with extremely useful kinetic information for studying
the details of a reaction mechanism.

The other technologies for studying transients include: Resonance Raman, ESR/Spin Traps, and Chemically Induced Nuclear Polarization (CIDNP). An enhanced Raman signal can be observed if the probe coincides with absorption band of the transient. This allows for the observation of two species with different Raman bands, which have overlapping UV-Vis absorption spectra, as well as provides detail about transient structure. ESR and CIDNP both are helpful for kinetic study.

Supercritical Fluids (SCF)

Physical Properties of Supercritical Fluids

If the temperature and pressure of a single component substance are increased until the "critical point" is reached (where \( P = P_c \) and \( T = T_c \)), many physical properties change abruptly and large fluctuations in density occur, leading to "critical opalescence" and the like (Figure 3). The substance in question cannot be regarded simply as liquid or gas but is still considered to be a single-phase fluid. Our interest is in the "super-critical fluid" region where \( P > P_c \) and \( T > T_c \). In this region, the substance exists as a single phase but having some of the advantageous properties of both gas phase and liquid phase. Table 1 shows that the range of bulk properties of supercritical fluids are between the range of gas and the range of liquid. Its similarity to liquid in density gives supercritical fluid appreciable power to dissolve other substance, while the diffusion coefficient of supercritical fluid is much larger than that of regular liquids. The low viscosity of supercritical fluids is beneficial to mass transport.\(^{11}\)

The most attractive supercritical region is \( 1 < T/T_c < 1.1 \) and \( 1 < P/P_c < 2, \)\(^{12}\) where is a compressible region. In this region, the unique and very applicable physical
properties (density, viscosity, diffusion coefficient, etc.) may be modified easily by small changes in temperature or pressure for specific tasks. For example many supercritical fluids have excellent but adjustable solvating powers, while having near-gaseous mobility. The properties of supercritical fluids make some of them excellent solvent extraction media as well as alternative reaction media. Since they are easily and continuously tunable on the bulk physical properties of the fluid (i.e. density, viscosity, dielectric constant), with small changes on temperature and pressure, thus this allows studies of chemical reactions in a tunable solvent environment from gas-like to liquid-like.

Table 1

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<th>Bulk Properties of Supercritical Fluids</th>
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<tr>
<td><strong>Density (g/cm³)</strong></td>
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<tr>
<td>Gas</td>
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<tr>
<td>Supercritical Fluids</td>
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<tr>
<td>Liquid</td>
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<tr>
<td>10⁻³</td>
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<tr>
<td>0.1~1</td>
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<tr>
<td>1</td>
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<tr>
<td><strong>Viscosity (g/cm•s)</strong></td>
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<tr>
<td>10⁻⁴</td>
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<tr>
<td>10⁻³~10⁻⁴</td>
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<tr>
<td>10⁻²</td>
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<tr>
<td><strong>Diffusion Coefficient (cm²/s)</strong></td>
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<tr>
<td>10⁻¹</td>
</tr>
<tr>
<td>10⁻³~10⁻⁴</td>
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**Supercritical CO₂ (SC CO₂)**

Among a limited number of supercritical fluids commonly used (e.g. SCF water, SCF ethane), supercritical CO₂ has attracted a lot of attention, due largely to the near ambient critical temperature and the environmentally benign characteristics of the fluid. Carbon dioxide becomes critical at close to ambient temperature 31.3°C and at 72.9 times atmospheric pressure. Figure 4 shows the critical point in Temperature-Pressure phase diagram of carbon dioxide. Pressure-Temperature phase
Figure 3. Generic Temperature – Pressure Phase Diagram of a Substance.

Figure 4. Temperature – Pressure Phase Diagram of Pure CO\textsubscript{2}.\textsuperscript{13}
The density-pressure relationship of supercritical CO$_2$ at two temperatures (35°C and 50°C) are shown in Figure 5. At 35°C, the density of supercritical CO$_2$ is liquid-like (0.8 g/cm$^3$) at high pressure (160 bar), which is comparable to many regular organic solvents. In the high-pressure region, the density of supercritical CO$_2$ decreases gradually as the pressure reducing. Then it sharply decreases when pressure is below 100 bar, which is a compressible region close to critical point. Finally, the density reaches 0.25 g/cm$^3$ at 73 bar. At 50°C, the density is lower than 35°C and the decrease of density with pressure decreasing from high to low, is more gradual. This tunability provides the tremendous potential to control bulk density of supercritical CO$_2$. A complete range of relationship of Pressure-Temperature-Density was given by Manivannan and Sawan. Figure 5.

Density Tunability in Supercritical CO$_2$. 

![Diagram showing the density-pressure relationship of supercritical CO$_2$ at two temperatures (35°C and 50°C).](image)
In addition to tunability of bulk properties, supercritical CO₂ can be worked at an ambient temperature, avoiding using conventional organic solvents, thus has no detrimental effects on environment. It is natural, colorless, odorless, tasteless, non-flammable, non-toxic, and inexpensive and in the supercritical phase has extremely low viscosity. Besides above, the use of supercritical CO₂ generally offers following benefits for both heterogeneous homogeneous reactions in practice: 1) easy to remove solvent; 2) enhanced diffusivity for solute; 3) higher yield and selectivity.

There has been a certain number of reports of experimental investigations and computational studies on chemical reactions in supercritical fluids. Among these studies, photochemical and photoinduced reactions in supercritical CO₂ attract a lot of attentions. Reaction chemistry (yields, rates and selectivities) is usually associated with the solvent effect of supercritical CO₂. The studies also include the photophysical and photochemical phenomena such as fluorescence quenching, charge-transfer and exciplex formation in supercritical CO₂.¹⁷

Tanko and co-workers reported the viscosity dependent behavior of geminate caged-pairs in supercritical fluid solvent.¹⁸ They studied the free radical chlorination of cyclohexane in both conventional and supercritical carbon dioxide solvents. The extension of the chlorine atom cage effect observed for this system in supercritical CO₂ could be predicted from extrapolations of conventional solution data. This suggested no distorting of the cage effect in supercritical CO₂. These research results lead the way to the potential utility of supercritical CO₂ as a versatile and tunable medium for achieving desired selectivity in high yields for free radical chlorination reactions.

Kaneco and co-workers studied photocatalytic reduction of CO₂ using TiO₂
powders in supercritical fluid CO$_2$. The reactants were irradiated in a stainless steel vessel at 9.0 MPa and 35°C. After reducing the CO$_2$ pressure to the ordinary state, no gaseous reduction products were observed. Formic acid was obtained only in aqueous solution. The optimal irradiation time for the production of formic acid was reported as 5 hours by authors. The results showed the addition of acidic solution rather than pure water was preferable for formic acid formation. Formic acid seems to be produced through the protonation of reaction intermediates on TiO$_2$ powders in solutions. The CO$_2$-reduction system described demonstrated practical value for efficient CO$_2$-conversion and fixation, storage of solar energy, and production of raw materials for the photochemical industry.

John E. Chateauneuf has been focusing his research interest on systematic study of homogeneous organic reaction chemistry in supercritical fluids as environmental benign media. Two classes of homogeneous reactions: Diffusion-controlled reactions and Kinetic-controlled reactions have been studied in supercritical fluids. In 1992, he and co-workers reported the laser photolysis of the hydrogen atom abstraction reaction of triplet benzophenone from 2-propanol and 1,4-cyclohexadiene in supercritical CO$_2$ reveals unusual pressure effects on abstraction rate constants. Monitoring reactivity close to the critical temperature (T$_c$) revealed that bimolecular rate constants increase sharply with a decrease in pressure, approaching the critical point. Kinetic investigations along an isotherm further removed from T$_c$ and predictive calculations on the pressure effect expected in supercritical CO$_2$ indicate that the enhanced reactivity is due to local substrate clustering.
Radical and Radical Ion in Supercritical Fluids

To understand chemical reactions in supercritical fluids, one key research direction is to identify and characterize the reaction intermediates as well as to learn how SCF solvent affects these intermediates, by solvent bulk properties and solvation dynamics. In a tremendous amount of organic reaction systems, free radical and radical ions are involved\(^{24}\). A complete review was given by J.E. Chateauneuf about reactions of free radicals in supercritical fluids.\(^{25}\)

Carbon anion is one of most important intermediates in a variety of organic reactions, specifically in photoinduced electron transfer reactions.\(^{26}\) Takahashi and coworkers studied an intermolecular electron transfer reaction between a biphenyl radical anion and pyrene in supercritical ethane by using pulse radiolysis\(^ {27}\). The second-order electron transfer rate constant was reported to be approximate constant in pressure range 55-133 bar\(^ {27}\). This result was attributed to solvent clustering or effect of pressure on reorganization energy.

In this thesis research, we tried to investigate three aspects: 1) the development of supercritical CO\(_2\) as an environmentally benign reaction medium and as a viable alternative to hazardous organic solvent, that may support polar and ionic systems; 2) the use of supercritical CO\(_2\) as a reagent for fixation of CO\(_2\), i.e., the use of CO\(_2\) as a C\(_1\) feedstock, and 3) the characterization of electron transfer reactivity under supercritical conditions. Research was conducted with the in-situ spectroscopic methods which are used to measure reaction rate constants and quantum yield, and by instrumental product analysis to determine efficiencies and selectivities. The beneficial of use of supercritical CO\(_2\) as a reactant and as a reaction medium in fixation of supercritical CO\(_2\) to aromatic hydrocarbon via photoinduced electron transfer carboxylation reaction, is yielding greater selectivity of product distribution.
The fundamentals of such enhancement were investigated. Results were compared to those literature reported results that were obtained in normal liquids, and analyzed in terms of our current understanding of individual factors that influence chemical reactivity in supercritical fluids.
EXPERIMENTAL SECTION

Materials

Anthracene (99%, M.W. 178.23) and phenanthrene (99%, M.W. 178.23) were commercially obtained from Aldrich, and recrystallized with 90% ethanol and 10% water mixed solvent. N,N-Dimethylformamide (DMF, HPLC grade, 99.9+%, M.W. 73.10) and N,N-dimethylaniline (DMA, 99.9%, M.W. 121.18) was also purchased from Aldrich as well as Acetonitrile (HPLC grade, UV cut off 190 nm) and used without further purification. Ethyl Alcohol (Absolute-200 proof) was purchased from AAPER ALCOHOL.

Carbon dioxide (SFC Grade) was obtained from Air Products and used without further purification.

Photoreactions and Apparatus

Photoirradiation of Aromatic Hydrocarbon-DMA-supercritical CO$_2$ System

Photoirradiation was carried out by use of a photochemistry setup consisting of an optical bench and one 1000W Xenon arc lamp obtained from Spectral Energy. Excitation wavelengths for the photoirradiation were selected by using a high intensity quarter meter grating monochrometer (Spectral Energy 350) with a large slit of 20 nm bandpass.

Photocarboxylation reactions of aromatic hydrocarbons in supercritical CO$_2$ were carried out by using a high-pressure apparatus. The system pressure was generated by a Teflon-packed syringe pump ISCO (Model 260D). The pressure was
monitored by a precision digital pressure gauge (Heise-901A) obtained from Dresser Industries, accurate to ±0.24 bar. The system temperature was controlled to ±0.2°C and monitored by an RTD temperature controller (Omega CN6070A) coupled with a Watlow firerod heating cartridge (Omega, 150W).

A high-pressure optical cell was used (Figure 6). It is made of 316 SS and is equipped with either quartz or sapphire windows at two ends of the cell, which are in 12.5 mm diameter and 5 mm in thickness. The calibrated volume of the optical cell is 2.54 ml. The quartz windows were sealed by Teflon O-rings.

A block-view of the whole high-pressure photoirradiation setup is shown in Figure 7.

![Stainless Steel High-Pressure Optical Cell](image)

Figure 6. Stainless Steel High-Pressure Optical Cell.

In the preparation of aromatic hydrocarbon solutions in supercritical CO₂, for example, a certain volume of acetonitrile solution of anthracene was added to the high-pressure optical cell. The cell was purged with a slow stream of nitrogen gas to remove the solvent acetonitrile as well as to eliminate trace amount of oxygen that would be a quencher in this photoreaction. Then the known amount of DMA and H-donor were added in cell by syringe. We make the concentration of DMA 100 times
higher than that of aromatic hydrocarbons to efficiently quench the singlet excited state of aromatic hydrocarbons. The cell was then sealed and filled with a known volume of CO₂. The concentration of anthracene was determined by known concentration and volume of acetonitrile solution, and the known volume of high-pressure optical cell system.

The high-pressure optical cell was thermostated at desired temperature before the photoirradiation. After the photoirradiation, the system was degassed by bubbling CO₂ through the acetonitrile solvent. Then reaction mixture was dissolved and washed out by acetonitrile solvent. The two portion of acetonitrile solution were combined to make a known volume of solution in 10ml volumetric flask, for further product analysis.

Photoirradiation for Aromatic Hydrocarbon-DMA-ACN (or DMF) System

The solution of acetonitrile (or dimethylaniline) that contains 0.025M
anthracene (or phenanthrene) and 0.5M DMA was placed in a quartz cuvette with 1cm optical pathway. The cuvette was screw capped to keep CO$_2$ pressure. Before the photoirradiation, the CO$_2$ was bubbled through the solution to expel dissolved O$_2$ make the solution system saturated with carbon dioxide. During the photoirradiation, the reaction process was monitored by Beckman DU 7400 UV-vis spectrometer. After photoirradiation, the reaction mixture was diluted into volumetric flask for further product analysis. For ACN system, both with and without hydrogen donor were studied.

In both high-pressure and regular solvent systems, the photoirradiation time was usually variable from 0.5 hour to 12 hours.

**Influence of Different Hydrogen Donor on Yield and Selectivity**

Cyclohexane, 1,4-cyclohexadiene and 2-propanol were selected as hydrogen donors. A small amount of different donor was injected in cell or cuvette just before the photoirradiation, since they are very volatile. Contribution of hydrogen donors on yield and selectivity of reaction were studied.

**Preparation of Chemicals**

**Synthesis of 9,10-Dihydro-9-anthracenecarboxylic Acid**

9,10-Dihydro-9-anthracenecarboxylic acid (I) has been prepared by the Birch reduction$^{28}$ of 9-anthracenecarboxylic acid, as illustrated by Figure 8.

This procedure was developed by referring the reductive synthesis of 1,4-dihydrobenzoic acid from benzoic acid.$^{29}$ 3g (0.014 mole) of 9-anthracene-carboxylic acid was added to 16.7 ml of anhydrous ethanol in a 500ml three-necked flask equipped with a magic stirrer and with loose cotton plug in the side necks.
After the 9-anthracene-carboxylic acid was dissolved, 100ml of liquid ammonia was added to the stirred solution. Then 1.1g of sodium was added in small pieces. When about one-third of the sodium has been added, the white sodium salt of the acid precipitated, and there was strong foaming of the reaction mixture. After all sodium has been consumed, the blue color of reaction solution disappeared. Then 2.4g of ammonium chloride was added cautiously. Keep stirring the mixture for additional hour and allow it stand until the ammonia has evaporated.

The residue was dissolved in 50ml of water. The solution was poured onto 30g of ice and acidified to a pH of about 4 by dropping of 10ml 6M hydrochloric acid. The resulting yellow mixture was extracted with three 30ml portions of peroxide-free ether, and the combined extracts were washed with 20ml of a saturated aqueous solution of sodium chloride and dried over about 1g of anhydrous magnesium sulfate. The ether solution is separated from the drying agent and concentrated at room temperature by rotatory evaporator. Keep the ether solution in refrigerator until the colorless crystal formed from light yellow mother-liquor. Colorless crystal was collected by quick filtration. Weight 2.35g (79% yield). M.P. 298 °C. H-NMR was obtained as shown in Figure 9. The product was photosensitive and sealed with nitrogen.
Synthesis of 9-Phenanthrenecarboxylic Acid

9-Phenanthrenecarboxylic acid was prepared by hydrolysis of 9-cyanophenanthrene which was obtained from Aldrich (97%), following the procedure described by Neckers\textsuperscript{30}. 1g (4.8 mmol) of 9-cyanophenanthrene was dissolved in 20ml diethylene glycol containing 1g NaOH. The mixture was refluxed for 5 hours. After cooling down in room temperature, 25ml diluted HCl was added into reaction mixture. The filtered white precipitate was dried in vacuum at room temperature, then recrystallized with anhydrous ethanol to form colorless crystal. (Yield 74%, mp. 249 °C, literature\textsuperscript{31} mp. 252°C). The product was kept in dark and sealed with nitrogen.

Synthesis of 9,10-Dihydro-9-phenanthrenecarboxylic Acid

9,10-Dihydro-9-phenanthrenecarboxylic acid (V) was obtained by photolysis of phenanthrene-9-carboxylic acid obtained by procedure described as above. 4ml of DMF solution with 0.01M phenanthrene-9-carboxylic acid and 0.02M DMA, was placed in a quartz cuvette with a screw-cap. Solution was purged with nitrogen gas for 10 minutes and sealed. After 10 hours irradiation at 358 nm, solvent was evaporated in vacuum at room temperature. The residue was dissolved in acetonitrile and separated by TLC and HPLC (acetonitrile as solvent system, flow rate 0.5 ml/min, 9,10-dihydro-phenanthrene-9-carboxylic Acid eluted at 1.28 minute, phenanthrene-9-carboxylic acid eluted at 1.98 minute). The product was identified by NMR.
Figure 9. $^1$H NMR Spectrum of 9,10-Dihydro-9-carboxylic Anthracene Acid.
Product Analysis by HPLC

The majority of the product analysis studies described above were performed using HPLC. Perkin-Elmer Series 4 Liquid Chromatograph was employed as routine HPLC analytical instrument, with LC-95 UV-visible Spectrometer Detector, and LCI-100 Laboratory Computing Integrator. Reversed-phase column (from α-Chrom, 3mm x 25cm) packed with C18 was equipped as stationary phase. Acetonitrile (Aldrich, HPLC grade, UV cutoff 190 nm), and Mili-Q water were used as bi-solvent system mobile phase. UV detector was set at 268nm. For quantitative analysis of aromatic acid-dihydroaromatic acid system, acetonitrile was used as mono-solvent. For analysis of reaction products of photocarboxylation, the following gradient (Table 2) was used.

Table 2
Condition Parameters for HPLC Product Analysis

<table>
<thead>
<tr>
<th>Elution time (min.)</th>
<th>Flow rate (ml/min)</th>
<th>Percentage of Acetonitrile</th>
<th>Percentage of H₂O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.0</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

Laser Flash Photolysis Experiments (LFP)

The nanosecond LFP experiments were performed by using laser excitation perpendicular to monitoring source—a pulsed 1000W xenon lamp. The block picture is shown in Figure 10. Laser excitation at 266nm or 355nm (~10mJ) was provided from a Quanta Ray Nd: YAG with a pulse width ~6ns. Transient absorption signal
collected by a Tektronix 7912 AD digitizer and a VAX-11/780 was employed as experimental controller and computation analyzer. This LFP apparatus and operational details have been previously described by J.E. Chateauneuf.\textsuperscript{21,32} The excitation condition parameters such as time delay were set for individual experiment.

In general, all absorption spectra were obtained using solutions with 0.6–0.9 O.D (Cary 219 UV-vis spectrometer) at the laser excitation wavelength. Cutoff filters were used at all wavelengths greater than 420nm to eliminate overtones.

Figure 10. Laser Flash Photolysis Apparatus.
RESULTS AND DISCUSSIONS

Monitoring Reaction Progress by UV-vis Spectroscopy

The absorption characteristics of organic molecules in the UV region depend on the electronic transitions that can occur and effect of the atomic environment on the transitions. The various transitions that can occur are summarized in Figure 11.

\[
\begin{align*}
\text{Antibonding } \sigma (\sigma^*) \\
\text{Antibonding } \pi (\pi^*) \\
\text{Nonbonding } n (\rho) \\
\text{Bonding } \pi \\
\text{Bonding } \sigma
\end{align*}
\]

Figure 11. Electronic Energy Levels and Transitions.

The system we studied here contains mainly aromatic compounds, which have absorption bands in the ultraviolet region. These bands originate from \( \pi \rightarrow \pi^* \) electron transitions (heavy arrow in Figure 11), i.e. the promotion of an electron from a \( \pi \)-bonding orbital to an antibonding (\( \pi^* \)) orbital as shown in Figure 12.

In Figure 12, (a) is bonding orbital where both \( \pi \) electrons occupy. A bonding \( \pi \) orbital has only one nodal plane of molecular skeleton. (b) is antibonding orbital which has an additional nodal plane perpendicular to the plane of the molecule and
bisecting the C-C bond. That is, the orbitals occupied by the π electron in the ground state and in the excited state as shown in Figure 12 the dark and white areas are regions of maximum electron density. The antibonding π electron no longer contributes appreciably to the overlap of the C-C bond and negates the bonding power of the remaining unexcited π electrons. The light energy absorbed by a species depends on the energy difference between the ground state and the excited state. The excess energy in the excited state may result in dissociation or ionization of the molecule, or it may be reemitted as heat or light such as fluorescence and phosphores. So for our photoirradiation experiment, we have to control the concentration of reaction mixture so that there is excess light energy to process the reaction.

![Figure 12. π → π* Transition.](image)

UV-vis spectra of anthracene and phenanthrene were experimentally obtained from Beckman DU7400 UV-vis spectrometer, and well agree with literature (NIST Chemistrybook).

Characteristics of the spectra of aromatic molecules are B band and E band. B band usually is a broad absorption band containing multiple peaks or fine structure, in the near-UV region. The fine structure arises from vibrational sublevels affecting the electronic transitions. Such fine structure may be absent if the aromatic compounds are substituted, or destroyed in polar solvent due to the interaction between solvent and solute. The other characteristic of aromatic compound is E band.
(ethylenic band), including E₁ and E₂ bands. Linear molecule anthracene has E₁ band at 256 nm (Figure 13) and E₂ band at 375 nm, which swaps the B band. The angular molecule phenanthrene has a three-band spectrum with E₁ band at 256 nm, E₂ band at 275 nm and B band at 330 nm (Figure 14).

Figure 13. UV-vis Spectrum of Anthracene in Acetonitrile.

The spectrum of N, N-dimethylaniline also has been obtained experimentally. N, N-dimethylaniline can be treated as bulky substitution in the ortho position of benzene, which causes a hypsochromic shift in the E₂ band with a significant reduction in ε_{max}. This is due to the interaction between the nonbonding electron pair of a heteroatom N attach to the ring and the π electrons of the ring is most effective when the p orbital of the nonbonding electrons is parallel to the π orbitals of the ring. λ_{max} of DMA is at 251nm as show in Figure 15.
Figure 14. UV-vis Spectrum of Phenanthrene in Acetonitrile, [PHN] = 0.0005M.

SC CO₂ does not have any significant absorption band in UV-vis region. The spectra of reaction mixtures have been obtained at the beginning of photoirradiation and after 2-hour photoirradiation (Figure 16a and 16b). The UV-vis spectrum of 9,10-dihydro-9-anthracenecarboxylic acid is shown in Figure 17. Since the attached group on the ring (-CO₂H) and hydrogenation breaks the three-ring π bond, both cause the absorption band to move toward short wavelength (higher energy). After the photolysis, the absorptivity on band 320~360nm was reduced.
Figure 15. UV-vis Absorption Spectrum of N,N-dimethylaniline in Acetonitrile.

Figure 16. UV-vis Spectra of Reaction Mixture, Pressure=1800psi, Temperature=35°C: (a) Before Photoirradiation; (b) After 2-Hour Photoirradiation at 366nm.
Figure 17. UV-vis Spectrum of 9,10-Dihydro-9-anthracenecarboxylic Acid.

Reaction Products Analysis and Separation by HPLC

A reversed-phase C₁₈ column was employed to separate the aromatic hydrocarbons. In the reversed-phase method, the most polar component appears first, and increasing the mobile phase polarity increase the elution time. Figure 18 is a typical HPLC chromatography for quantitative analysis of reaction system. Peaks in Figure 19 were identified by the pure compounds respectively which were obtained by alternative ways. This chromatography was obtained by an isocratic elution at room temperature, which means a single solvent of constant composition (acetonitrile: water = 90:10 in volume) was employed.

For higher separation efficiency, we employed two solvent systems that differ significantly in polarity (Polarity index $P'$: Acetonitrile = 5.8, water = 10.2³⁴). After elution was begun, the ratio of solvents was varied in a programmed way, sometimes continuously and sometimes in a series steps. This method is so-called gradient elution. The ratio change for this experiment was following the Table II. From Figure
19, the separation efficiency was greatly enhanced. However, the retention time (at 2.473 min) of DMA and amine adduct still could not be separated under this condition.

Figure 18. HPLC Spectrum of Anthracene-DMA-2-Propanol Reaction Products Mixture.

Conditions and yields of the photocarboxylation of anthracene, phenanthrene and pyrene with N, N-dimethylaniline (DMA) in presence of hydrogen donor cyclohexane in supercritical CO₂, are summarized in Table 3. Unlike similar reactions carried in regular solvents in the literature, such photocarboxylation reactions have higher selectivity and less side reactions. The possible trace amount of side products such as radical coupling product (III) and 9,10-dihydroanthracene (IV) could be too small for an unambiguous examination under this experiment condition. 9,10-Dihydroanthracene may be consumed during photocarboxylation process as a hydrogen donor.
The selectivity of dihydrocarboxylic acid for anthracene and phenanthrene are very close. Because the dihydrocarboxylic acid and amine adduct are the main products. Since the absorption band of phenanthrene at 366nm is much weaker than that of anthracene. The photoreaction speed of anthracene is much faster than phenanthrene. The selectivity of carboxylic acid in phenanthrene system is slightly higher than that in anthracene. This could be due to the byproduct formation at the initial state of photoirradiation.

The aromatic carboxylic acid products were qualitatively and quantitatively identified by comparison with respective authentic samples we synthetically obtained as described above. The existences and structures of (II) and (VI) were indicated by their experimental observation and spectral properties. Due to interference of DMA, the $^1$HNMR spectrum of (II) has a very good agreement on some peaks with literature$^{33,35}$: 82.75 (singlet, originated from N-CH$_3$), 86.7 (weak, originated from $p$-C$_6$H$_4$-), and multiplet at 87.2 originated from aromatic protons. We could not obtain
significant signals: δ3.90 (doublet, originated from C_{10}-H_{2}), δ5.1 (triplet, originated from C_{9}-H). The possibility of compounds (II) and (VI) will be discussed in results section. The total recoveries for both anthracene and phenanthrene system are over 100%, which might be caused by the shortcoming of our product analysis: 1) the isolated DMA adducts for both anthracene and phenanthrene were not available, we chose anthracene and phenanthrene as external standard in HPLC for their DMA adducts respectively, obviously there exists discrepancy on UV-vis absorptivity; 2) even the DMA was evaporated by vacuum, it still has interference with these adducts due to the high boiling point of DMA. The peak at the retention time of DMA on HPLC still significantly exists after evaporation.

Table 3

<table>
<thead>
<tr>
<th>ArH</th>
<th>Photoirradiation time, h</th>
<th>Consumed ArH %</th>
<th>Yields of products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>3</td>
<td>88</td>
<td>(I) 32, (II) 77</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>3</td>
<td>90</td>
<td>(V) 34, (VI) 75</td>
</tr>
</tbody>
</table>

* [ArH] = 1.0×10^{-4}M, [DMA] = 0.01M, [Cyclohexane] = 0.01M, Temperature = 35.0± 0.2°C, Pressure =1700 ± 20 psi.

Factors Affecting Photoreaction Pathway

Solvent Effects on Photoreaction

Solvent is one of the major factors that are considered to affect the reaction pathway. The results in Table 4 indicate that reaction in supercritical CO_{2} has higher yield and selectivity than others when a good hydrogen donor is added. As reported by
Tazuke et al.

our results show that acetonitrile is an unfavorable solvent that produces low yield and selectivity. This is because acetonitrile is neither a good hydrogen donor nor a good electron donor. Also, some side reactions may occur in acetonitrile such as coupling, for example, compound (III) and (VIII).\textsuperscript{35} Because the dipolar aprotic solvents are good electron donor, DMF is a suitable regular solvent as expected.

Figure 20. Anthracene Dimmer (Compound VIII)

Table 4
Solvent Effects on Photocarboxylation of Anthracene With DMA

<table>
<thead>
<tr>
<th>solvent</th>
<th>photoirradiation time, h</th>
<th>consumption of anthracene, %</th>
<th>yield of dihydrocarboxylic acid, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile\textsuperscript{a}</td>
<td>5</td>
<td>23</td>
<td>&lt;1</td>
</tr>
<tr>
<td>DMF\textsuperscript{a}</td>
<td>5</td>
<td>63</td>
<td>11</td>
</tr>
<tr>
<td>Supercritical CO\textsubscript{2}\textsuperscript{b}</td>
<td>5</td>
<td>87.3</td>
<td>34.5</td>
</tr>
<tr>
<td>Supercritical CO\textsubscript{2}\textsuperscript{b}</td>
<td>3</td>
<td>88.1</td>
<td>32.0</td>
</tr>
</tbody>
</table>

a. In regular solvents, [ArH] = 0.001M, [DMA] = 0.1M, room temperature.
b. T=35.0 ± 0.2\textdegree C, P = 1700 ± 20 psi, [cyclohexane] = 0.01M, [DMA]=0.01M, [ArH]=1.0x10^{-4}M.
Beside the environmental benefits of supercritical CO$_2$ as the reaction medium, as we discussed before, the solvent effect of supercritical CO$_2$ has been clearly documented as an important role in reaction chemistry, based on its physical and chemical properties. In this case, the photocarboxylation of aromatic hydrocarbons are bimolecular photoelectron transfer reactions. A complete understanding of solvent affect of supercritical CO$_2$ on this category of reactions requires study of the general bimolecular PET process as shown in Figure 21.

\[
\begin{align*}
A^* + D & \xrightarrow{k_{\text{diff}}} A^*/D \\
A^* & \xrightarrow{k_{\text{et}}} A^- + D^+
\end{align*}
\]

\[\text{Figure 21. The General Pathway and Intermediates in Bimolecular Photoinduced Electron Transfer Reactions in a Fluid Solvent.}\]

The excited state acceptor (A*) primarily forms an encounter pair A*/D with electron donor (D) as quencher. Two kinds of radical-pairs are generally considered as intermediates formed from encounter pair$^{36, 37, 38}$: the solvent-separated radical-ion pairs (SSRIP, A$^-(s)$D$^+$, Figure 22a) and the contact radical-ion pairs (CRIP, A$^-$D$^+$, Figure 22b). i.e. PET reaction between donor and acceptor lead to either exciplex formation or ionic dissociation, and finally leads to in cage coupling CRIP and out
cage coupling SSRIP. When quenching of $A^*$ via electron transfer is efficient, reaction occurs at or close to the diffusion-controlled limit. The further separation of SSRIP forms the fully separated or free radical ions ($A^- + D^+$). In the work presented in this thesis, separated free radical ion $A^-$ further form $CO_2$ adduct-carboxylated radical anion. Here $A^-$ is a reductant of $A(CO_2)^+$. It should be noticed that there is a competing pathway following up formation of CRIP and SSRIP, and accompanying with most of separation processes, which is called Back Electron Transfer (BET). BET reactions in CRIP and SSRIP lead to regenerate ground state acceptor and donor, $(k_{eJ})_{cp}$ and $(k_{eJ})_{cp}$ respectively.

![Diagram of solvent separated radical ion pairs and contact radical ion pair.](image)

**Figure 22.** Solvent Separated Radical Ion Pairs and Contact Radical Ion Pair.

It was reported that only SSRIP played an important role in polar solvent.\(^{39}\) This was supported by the evidence, which clearly indicated that the CRIP reaction has higher electronic coupling matrix element and a smaller solvent reorganization energy than those of the SSRIP. When the radical ions are in contact, the orbital overlapping degree should be larger than when separated by a solvent layer. A simple cartoon representation is shown in Figure 22. Beside the solvent molecules between
radicals, interpenetration of outer shell solvent molecules surrounding the radical ions is diminished because of large separation distance, leads to higher overall solvation.

As indicated in Figure 21, the CRIP may solvate to form a SSRIP ($k_{\text{solv}}$). The SSRIP may separate to form free radical ions ($k_{\text{sep}}$), or desolvate to reform the CRIP ($k_{\text{solv}}$). Gould pointed out that the free energy of formation of both radical-ion pairs is function of solvent polarity.\(^{40}\) When the solvent dielectric constant is less than 7, the SSRIP is more than 0.1 eV higher in energy than the CRIP, and seems not to play any important role in bimolecular electron transfer reactions. The CRIP and SSRIP energies become equal when the solvent dielectric constant around 13. At higher polarity, the SSRIP energy is just a little lower than CRIP. When the dielectric constant of the solvent is increased, $k_{\text{solv}}$ and $k_{\text{sep}}$ increase, and $k_{\text{solv}}$ decreases.

Chitanvis applied Cavity Model toward understanding the solvation of ions and dipolar molecules in supercritical CO\(_2\).\(^{41}\) A generalization of Poisson's equation, a fourth-order partial differential equation, has been derived to describe the electrostatic behavior of polarizable, quadrupolar fluid, such as supercritical CO\(_2\). The result indicated that the quadrupolar portion of the disturbance created by an electrostatic probe in a polarizable quadrupolar fluid is localized to distance of about a bohr, while asymptotically the fluid behaves as a polarizable medium. Fairly good agreement was found between the theoretical predicted and the experimental determined dielectric constant for carbon dioxide. Kobelev et al\(^{42}\) reported that the dielectric constant ($\varepsilon$) of CO\(_2\) was determined at 293.17-348.11 K under pressures of 0.9-9.8 MPa and compared with theoretical predictions. At the critical point $\varepsilon = 1.261 \pm 0.005$ and the density is 0.468 g/cm\(^3\). From literatures, the polarity of supercritical CO\(_2\) seems unfavorable to form the solvent-separated radical-ion pair, which is further generated our target product-carboxylic acid.
However, beside the solvent-solute interactions, it is also well known that the addition of small quantities (1-5 mol%) of cosolvent greatly enhances solubility of organic solutes in supercritical fluids. Lu and coworkers\textsuperscript{43} studied the local dielectric constant around the solute in SC CO\textsubscript{2} with or without co-solvent, and they found significant difference between local dielectric constant and bulk dielectric constant calculated from homogeneous dielectric medium theory, which strongly suggests clustering of the solvent/cosolvent around the solute. This phenomenon is a result of enhanced solute-cosolvent interactions by spectroscopic studies. Such enhancement may lead to local composition enhancements (considerable 8 to 10 times large than the bulk composition).\textsuperscript{20, 25} The changes in local environment are controlled by short-range solvation interactions.\textsuperscript{25} In our investigation, dimethylaniline, 2-propanol, 1,4-cyclohexadiene and cyclohexane are added in as cosolvent (cosolute) as well as reactant. Since the rate of bimolecular and pseudo-first-order reactions are directly dependent on the molar concentrations of reactants, local enhancement of the concentration of one of the reactants may greatly differ from rate constants based on bulk concentration.

Figure 23 is a simplified picture representing the microstructure of solvent-solute (solvent-solute clustering) with or without cosolvent. This picture also shows that the other most important solvent property of supercritical CO\textsubscript{2}, which is local density argument. It is clarified that the local solvent density of supercritical fluids around a dilute solute may be significantly greater than the bulk density of the fluids by experimental\textsuperscript{25, 44}, theoretical investigation.\textsuperscript{45} The local density enhancements are short-range effects and not effects and not related to long-range fluctuations or other phenomenon related to criticality. Further work is required to determine whether the efficiency of photocarboxylation of aromatic hydrocarbons is affected by the local
density argument (or solvent-solute clustering) in supercritical CO$_2$, which would provide a completed supporting evidence for our proposed mechanism as discussed later in this thesis.

![Figure 23. The Microstructures of Solvent-solute Clustering With and Without Cosolvent.](image)

Influence of Reactant Concentrations

To focus on the effects of supercritical CO$_2$, the concentration of DMA was added in reactions, to completely quench all of excited aromatic hydrocarbon.

Besides affecting bulk density (Figure 5) that could have influence on solvation as mentioned before, increasing pressure of supercritical CO$_2$ is considerably a favorable condition as shown in Table 5. Since the photocarboxylation is competing with other side reactions, increasing concentration by increasing pressure of carbon dioxide likely pushes selectivity of the reaction toward carboxylation. In Figure 21, there is an equilibrium between aromatic carbon-centered hydrocarbon radical anion $A^-$ and the carboxylated radical anion $A$(CO$_2$)$_\circ$. A high carbon dioxide concentration would increase the concentration of the carboxylated radical anion by consuming the $A^-$ to reduce the steady-state concentration of $A^-$, thus
make the formation of BET product less likely. It is should be noticed that the percentage of consumed anthracene nearly kept constant, indicating that the consumption of aromatic hydrocarbons greatly depends on photoinititation. When increasing pressure of SC CO$_2$, the viscosity of SC CO$_2$ increases and polarity decreases, this makes less contact chance between aromatic hydrocarbons and DMA.

Table 5
Reactions at Various CO$_2$ Pressure at 35.0± 0.2°C*

<table>
<thead>
<tr>
<th>Pressure of CO$_2$, psi</th>
<th>Photoirradiation time, Hour</th>
<th>Consumption of ArH, %</th>
<th>Yield of dihydrocarboxylic acid (RCOOH), %</th>
<th>[RCOOH]/[consumed -ArH], %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>2</td>
<td>84.0</td>
<td>31.3</td>
<td>37.3</td>
</tr>
<tr>
<td>1700</td>
<td>2</td>
<td>86.0</td>
<td>32.0</td>
<td>37.2</td>
</tr>
<tr>
<td>2500</td>
<td>2</td>
<td>88.0</td>
<td>37.0</td>
<td>42.0</td>
</tr>
<tr>
<td>3500</td>
<td>2</td>
<td>87.0</td>
<td>47.0</td>
<td>54.0</td>
</tr>
</tbody>
</table>

* [ArH] = [Anthracene] = 1.0 x 10$^{-4}$ M, [Cyclohexane] = 0.01 M, [DMA] = 0.01 M.
The uncertainty for pressure is ± 20 psi

Influence of Various Hydrogen Donors

The primary purpose to add 2-propanol, 1,4-cyclohexadiene and cyclohexane is to use them as hydrogen donor. Although DMA and dihydro aromatic compounds could be hydrogen sources, the role of a suitable hydrogen donor was especially important when the photocarboxylation was carried out in aprotic supercritical CO$_2$. The effects of hydrogen donors are shown in Table 6. Agreeing with the results in regular solvents$^6,^{30}$, the results indicate that the yields are enhanced by choosing a suitable hydrogen donor that facilitates the forward reaction and suppresses BET.
It should be noted that the selectivity of carboxylic acid in presence of 2-propanol is even better than that in presence of 1,4-cyclohexadiene, while the latter is usually considered as a better hydrogen atom donor than the former. Thus the free radical anion $A^-$ is so easily protonated by 1,4-cyclohexadiene that it makes formation of carboxylated radical anion $A(CO_2)^-$ less possible. Consequently, the yield of carboxylic acid is not increased significantly.

Table 6

Effects of Various Hydrogen Donors*

<table>
<thead>
<tr>
<th>H-donor</th>
<th>Consumption of phenanthrene, %</th>
<th>$[\text{RCOOH}]/[\text{consumed-ArH}]$, %</th>
<th>Consumption of anthracene, %</th>
<th>$[\text{RCOOH}]/[\text{consumed-ArH}]$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>78.1</td>
<td>31.5</td>
<td>88.1</td>
<td>34.1</td>
</tr>
<tr>
<td>2-propanol</td>
<td>81.3</td>
<td>52.7</td>
<td>&gt;99</td>
<td>57.0</td>
</tr>
<tr>
<td>1,4-hexadiene</td>
<td>82.0</td>
<td>51.9</td>
<td>&gt;99</td>
<td>56.2</td>
</tr>
</tbody>
</table>

* $[\text{PHN}]=[\text{ArH}]=0.001$M, $[\text{DMA}]=0.01$M, $[\text{H-donor}]=0.01$M, Temperature=$35.0 \pm 0.2^\circ$C, Pressure= 2000 ± 20 psi, 2-hour photoirradiation.

Mechanism of Reductive Photocarboxylation

Now we can present a mechanistic scheme of the photocarboxylation as shown in Figure 24. Here we chose phenanthrene as the cleanest reaction system (no coupling, dimerization etc.) for detailed study. Although the triplet excited state of phenanthrene $^3\text{PHN}^*$ also exists in reaction system, free radicals are generated mainly from the electron transfer process between singlet excited state $^1\text{PHN}^*$ and DMA. The photoinduced electron transfer reaction is to be considered as an initializing and fast step in the whole process, which is at diffusion-controlled rate$^{46}$. Inomata$^{47}$
observed the evidence of pyrene-DMA exciplex in supercritical CO$_2$ by fluorescence spectroscopy. The formation rate and structure of anthracene-DMA exciplex were found to differ with respect to polarity of solvent.$^{48}$

Toki$^{49}$ and coworkers studied the photofixation of CO$_2$ in styrene-triethylamine system. They pointed out that CO$_2$ reacted with the styrene radical anion effectively to form carboxylic acids instead of with styrene-triethylamine exciplex. By analogy with the photocarboxylation reactions in regular solvent, addition of CO$_2$ to the radical anion PHN$^-$ which forms PHN(COO)$^-$, should be faster than hydrogen abstraction. CO$_2$ addition is considered to be diffusion-controlled reaction theoretically, while hydrogen transfer was investigated as a kinetic controlled reaction in both regular solvents$^{50}$ and supercritical fluids.$^{51}$ The experimental results discussed above are consistent with this proposed mechanism.

Figure 24. Proposed Reaction Paths for Photocarboxylation of Phenanthrene in Supercritical Carbon Dioxide.
Although we could not obtain direct evidence for formation of 4-(9,10-dihydro-9-phenanthrenyl)-N,N-Dimethyl-benzenamine(VI) during photocarboxylation reaction as coupling product of phenethrene and DMA. But based on following facts, we agree with Tazuke's results: 1) the selectivity of acid is far below 100%, which means some other products must have consumed aromatic hydrocarbons, 2) After evaporated most of unreacted DMA, the residue was colorful (green in chloroform, violet in acetonitrile), the color could not be from either anthracene or DMA. However, anthracene and phenanthrene are good chrome-group and DMA is a good auxo-chrome group, which implies that their coupling adductive should be colorful, and 3) the H\textsuperscript{1}NMR results partially agree with Tazuke's report. DMA has a well-known coplanar structure between the dimethylamino group and the benzene ring in solid state as well as in solution (Figure 25a). Therefore, odd electrons of the radical cations would populate the benzene ring with most probability at ortho and para positions. Figure 26 shows that there are three resonance structure for radical cation DMA\textsuperscript{+}. The radical ions coupling reaction of DMA\textsuperscript{+} with A\textsuperscript{−} at the para position is much favorable, because the steric hindrance is much less and para DMA\textsuperscript{+} is the most active resonance structure.

Figure 25. Steric Structure of DMA and its Possible Coupling Products with Aromatic Hydrocarbon Anion Radicals.
Figure 26. Resonance Structures for DMA Radical Cation.

Transient Absorption Spectra

Laser flash photolysis of phenanthrene-DMA system was carried out in both acetonitrile and supercritical CO₂. Comparing with transient spectra of pure phenanthrene in acetonitrile (Figure 27), in PHN-DAM acetonitrile system (Figure 28), we identified that the strong absorption band at 420nm with a shoulder peak at 395nm are attributed to the triplet excited state of phenanthrene, as well as a weak broad band at 485nm. Since DMA should not have any absorption at the excitation light at 355nm. The other mediate broad band at 470nm is considered the absorption of transient radical anion PHN⁻. We plotted spectra at different time intervals after the laser pulse. A difference in the character of the decay at 420nm and 470nm indicated the presence of at least two transient species. We replaced the DMA with
triethylamine in presence with anthracene in acetonitrile. We still can observe such a broad band at 470nm (Figure 29). This provided the evidence for us that such band does not belong to DMA transient species.

By analogy with the spectra of PHN-DMA in acetonitrile (Figure 28), we believe that the PHN⁻ exists in PHN-DMA-supercritical CO₂ system (Figure 30) as transient. The weak absorption band could be attributed the fast quenching of radical anion by CO₂ leading to another carboxylic anion. But we do not have any spectra evidence about such a carboxylic phenanthrene anion.

![Figure 27. Transient Absorption Spectra of Phenanthrene With DMA in Acetonitrile With 355nm Laser Excitation.](image-url)
Figure 28. Transient Absorption Spectra of Pure Phenanthrene in Acetonitrile With 355nm Laser Excitation.

Figure 29. Transient Absorption Spectrum of Anthracene With Triethylamine in Acetonitrile With 266nm Laser Excitation.
Figure 30. Transient Absorption Spectra of Phenanthrene With DMA in Supercritical CO₂ With 355nm Laser Excitation.
CONCLUSIONS

In this investigation, supercritical CO$_2$ has been used as an environmental benign solvent and C$_1$ feedstock. 9,10-Dihydro-9-anthracenecarboxylic acid and 9,10-dihydro-9-phenanthrenecarboxylic acid were obtained by photoirradiation. In the range of aromatic hydrocarbon concentration $10^{-5}$M~$10^{-3}$M, the consumption of phenathrene and anthracene in supercritical CO$_2$ under experimental condition are 78%~–90% and 88%~–>99% respectively. The highest selectivity of 52.7% and 57.0% respectively were observed. The experimental results of yields and selectivities for carboxylate products shown that reductive photocarboxylation of aromatic hydrocarbons are reasonably more efficient in supercritical CO$_2$ than that in regular organic solvents. The high yield is mainly attributed to the solvent properties of supercritical CO$_2$ and the fact that supercritical CO$_2$ is also a reactant reduces the pathways to byproducts.

Such a CO$_2$ fixation is initiated by using photoinduced electron transfer (PET) reaction where aromatic hydrocarbon acts as electron acceptor and amine is an efficient electron donor. In photo-initiate step, an aromatic carbon-centered radical anion was produced as reaction intermediate. In this case, addition of hydrogen donors is necessary to convert the reactive intermediate to final products. Choosing different hydrogen donors affects the both yields and selectivities of carboxylic acids.

Increasing system pressure from 1200psi to 3500psi slight increases the yields, but significantly increase the selectivities of carboxylic acids. By Laser-Flash Photolysis, a new transient species was observed and maybe due to as radical anion by comparing known transient spectra. Mechanistic and spectroscopic evidences are
consistent with the involvement of carbon-centered aromatic radical anions in the photocarboxylation reactions studied.
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