# Photochemical fixation of supercritical carbon dioxide: the production of a carboxylic acid from a polyaromatic hydrocarbon

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## Abstract

We present our initial results on the use of supercritical carbon dioxide as both a reactant and as a reaction medium to photo-chemically produce carboxylic acids from polycyclic aromatic hydrocarbons via radical anion intermediates. In the present work, we have found that photolysis of anthracene in supercritical carbon dioxide produces up to 57% yield of 9,10-dihydroanthracene-9-carboxylic acid in the presence of appropriate electron and hydrogen donors. This is in stark contrast to the lack of carboxylic acid formation in conventional non-polar aprotic solvents. Additionally, we have found no evidence that under reaction conditions similar to those necessary for radical anion fixation of carbon dioxide that carbon-centered free radicals produce carboxylic acids. © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Currently, there is great interest in the use of supercritical carbon dioxide (SC $CO_2$) as a more environmentally responsible alternative to conventional organic solvents for use in chemical production and materials processing (Noyori, 1999; Jessop and Leitner, 1999). There is also significant interest in the use of $CO_2$ as an inexpensive environmentally friendly $C_1$ feedstock (Jessop et al., 1995; Fujita, 1996). That is, to use $CO_2$ as a carbon source for the production of valuable chemical commodities.
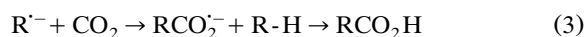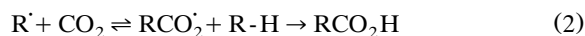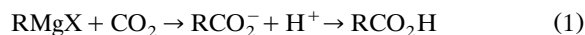
In this report, we present our initial results of the use of SC $CO_2$ as both a reactant and as a reaction medium for the production of carboxylic acids. Specifically, we have photochemically synthesized a carboxylic acid from an aromatic hydrocarbon via production of an aromatic radical anion produced from a photo-induced electron transfer reaction. We present a comparison of the percent yield of carboxylic acid production under SC $CO_2$ conditions to those produced in conventional solvents.

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There are two major impediments to using $CO_2$ as a chemical reagent. One is that $CO_2$ is only reactive towards a few chemical substrates. Second, when using $CO_2$ as a reagent in conventional liquids, the concentration of $CO_2$ is limited by its solubility in the reaction medium. We have overcome the second limitation by using $CO_2$ as the reaction medium. However, for the specific case of using $CO_2$ as a $C_1$ feedstock, to overcome the first difficulty requires the use of an extremely reactive (nucleophilic) substrate. The most well known example of such a reactive reagent is the Grignard reagent, which is essentially a carbanion, that will nucleophilically attack $CO_2$ to produce carboxylate, which may subsequently produce carboxylic acid [Eq. (1)]. However, $CO_2$ fixation of the Grignard reagents is, as mentioned, dependent on $CO_2$ solubility in conventional solvents.

Another potential 'reagent' that may react with $CO_2$ to produce carboxylic acids are carbon-centered free radicals [Eq. (2)]. When using $CO_2$ as a solvent, it may be possible to have carbon-centered free radicals react with $CO_2$ to produce carbonyloxyl radicals ($RCO_2^{\cdot}$), which in the presence of a hydrogen atom donor, may then result in carboxylic acid production [Eq. (2)]. It is well known that carboxylation of carbon-centered free radicals is not favored under normal reaction conditions, e.g. in organic solvents. In fact, alkyl and aryl carbonyloxyl radicals are known to decarboxylate on the picosecond to nanosecond time-scale, respectively (Chateauneuf et al., 1987, 1988a,b).

$$RMgX + CO_2 \rightarrow RCO_2^- + H^+ \rightarrow RCO_2H \qquad (1)$$

$$R^{\cdot} + CO_2 \rightleftharpoons RCO_2^{\cdot} + R\text{-}H \rightarrow RCO_2H \qquad (2)$$

$$R^{\cdot -} + CO_2 \rightarrow RCO_2^{\cdot -} + R\text{-}H \rightarrow RCO_2H \qquad (3)$$

It is interesting to note, however, that when $CO_2$ or SC $CO_2$ is used as the solvent, Le Chatelier's principle would suggest a shift in the equilibrium for the first portion of Eq. (2). This could favor the carbonyloxyl radical, and if there was a sufficient amount of hydrogen atom donor present, carboxylic acid could possibly be formed (Hadida et al., 1997). We have explored this possibility by the generation of either methyl, phenyl or benzyl free radicals in SC $CO_2$ in the presence of a hydrogen atom donor, and as of yet, we have not been able to detect carboxylic acid as a product. However, we have been successful in the generation of carboxylic acids when we have generated radical anions in SC $CO_2$ in the presence of hydrogen donors, according to Eq. (3). In this report, we present carboxylic acid yields obtained under a variety of reaction conditions, and describe the reaction mechanism involved and the high-pressure methodologies used.

## 2. Materials and methods

### 2.1. Materials

Anthracene (99%), Aldrich (Milwaukee, WI), was re-crystallized with 90% ethanol and 10% water mixed solvent. Acetonitrile (HPLC grade, UV cut off 190 nm); cyclohexane; 1,4-cyclohexadiene; 2-propanol; *N*,*N*-dimethylaniline (DMA); Dimethylformamide (DMF), acetic acid, benzoic acid, benzylcarboxylic acid and dibenzylketone were also purchased from Aldrich (Milwaukee, WI) and used as received. Carbon dioxide (SFC grade, 99.99%) was obtained from Air Products (Allentown, PA) and used without further purification.

### 2.2. Equipment

A high pressure optical cell was used as the photoreactor. The high pressure optical cell was constructed of stainless steel, had approximately 3 ml capacity (1.7 cm optical path length) and was fitted with Suprasil quartz windows having mechanical seals of lead packing. The design, construction and operational use of our optical cells and high pressure apparatus have been described elsewhere (Roberts et al., 1992). Briefly, a model 901A Heise pressure gauge, Dresser Industries (Newtown, CT), was used to monitor pressure and an Omega (Stamford, CT, USA) Model CN-6070A temperature controller equipped with a cartridge heater and a platinum resistance thermometer was used to control temperature.

The apparatus used to deliver $CO_2$ to the high pressure optical cell consisted of the following components: a $CO_2$ gas cylinder, fitted with a diptube; a model 260D Isco (Lincoln, NE) high pressure syringe pump, thermostated with a water jacket and a Fisher Scientific (Pittsburgh, PA) ISOTEMP 1006s heater/chiller re-circulation bath. Connections to the photo-reactor (optical cell) were made with HIP (Erie, PA) 1/16″ stainless steel high pressure tubing and high pressure (HIP) line valves fitted with Teflon o-rings.

Photoirradiation was carried out using a 1000 W xenon arc lamp, Spectral Energy (Westwood, NJ). Excitation wavelengths for the photoirradiation were selected using a high intensity quarter meter grating monochromator, Spectral Energy 350 (Westwood, NJ). UV-vis absorption measurements were performed using a Beckman DU 7400 spectrophotometer. ^{1}H-NMR experiments were performed using a JEOL (Peabody, MA) Eclipse 400MHz NMR spectrometer.

### 2.3. Procedure

Photolysis in the conventional solvents (acetonitrile or DMF) were performed in standard $1 \times 1 \times 3$-cm

quartz cuvettes that were fitted with screw-caps containing Teflon septa. The solutions were deaerated with $CO_2$ and bubbled with $CO_2$ during photolysis. UV-vis spectroscopy was used to characterize the reactants and solvents and to follow reaction progress. Supercritical $CO_2$ photolysis mixtures were prepared by addition of an appropriate amount of anthracene stock solution in acetonitrile to the high-pressure optical cell. This was followed by purging with a slow stream of nitrogen to remove solvent. Immediately prior to sealing the cell, DMA and the hydrogen donor were added and the cell was slowly purged with $CO_2$ and then loaded with liquid $CO_2$ from the Isco high pressure syringe pump and sealed. The cell was then heated to facilitate mixing and raise the contents above the critical point of the mixture. The high-pressure optical cell was thermostated at the desired temperature ($\pm 0.2°C$) before photoirradiation. After the irradiation, the cell was depressurized through acetonitrile solvent. The remaining contents of the high pressure optical cell were also recovered using acetonitrile, and the combined acetonitrile solutions were prepared for product analysis.

HPLC product analysis was performed using a Perkin-Elmer chromatograph (Norwalk, CT), Series 4 Liquid with LC-95 UV-vis spectrometer detector set at 268 nm, and LCI-100 laboratory computing integrator. Separations were performed using a reversed-phase 3 mm × 25-cm C18 packed column and gradient controlled acetonitrile/water was used as eluent. Authentic samples of 9,10-dihydro-anthracene-9-carboxylic acid (**I**) were prepared by standard Birch reduction of 9-anthracene-carboxylic acid (Kuehne and Lambert, 1973). Analytical data (NMR, IR, m.p.) of isolated photochemically generated samples of **I** agreed well with the authentic samples (Kuehne and Lambert, 1973). Authentic samples of **I** were also used for HPLC identification and analysis. Alkylcolbaloximes were prepared according a literature procedure (Schrauzer, 1967; Bakac and Espenson, 1987; Endicott et al., 1989).

## 3. Results and discussion

### 3.1. Background

In an initial communication in 1975 and then in a full paper in 1986 Tazuke and Ozawa reported some of the first examples of photofixation of $CO_2$ in a non-biological system (Tazuke and Ozawa, 1975; Tazuke et al., 1986). Specifically, they reported the first examples of reductive photocarboxylation of aromatic hydrocarbons, e.g. anthracene, phenanthrene, pyrene, to generate carboxylic acids. Photocarboxylation was observed upon irradiation of the aromatic hydrocarbons (A) in an aprotic polar solvent, such as dimethylformamide
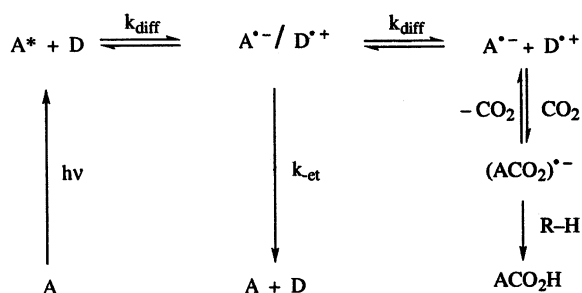


Scheme 1. Carboxylate anion radical formation.

(DMF) in the presence of an electron donating amine (D) and in the presence of $CO_2$. They found solvent polarity to be an important factor with carboxylation proceeding in DMF but not in THF, dioxane or *n*-hexane. These observations were consistent with a photo-induced electron transfer mechanism in which a photolytically excited state of an aromatic hydrocarbon (A*) may diffusionally encounter an electron donating amine (D) to produce a radical anion/radical cation encounter complex Kavarnos, 1993 (see Scheme 1). The encounter complex may either undergo back electron transfer and regenerate A and D, or solvent separate to produce free radical ions. In the presence of $CO_2$, $A^-$ nucleophilically adds to $CO_2$ to form a radical carboxylate ($ACO_2^-$), which will yield carboxylic acid products in the presence of a suitable hydrogen donor. Specifically for the case of anthracene, Tazuke and Ozawa reported (Tazuke et al., 1986) a 14% yield of 9,10-dihydroanthracene-9-carboxylic acid (I) [see Eq. (4)] following 2-h 366-nm irradiation of anthracene in $CO_2$ saturated DMF solution containing *N,N*-dimethylaniline (DMA) as the electron donor. In Tazuke and Ozawa's DMF experiments, isotopic labeling demonstrated that the solvent acted as the hydrogen source. However, comparable experiments using acetonitrile as solvent did not result in significant carboxylic acid production (Table 1). This is due to the poor hydrogen donating ability of acetonitrile.

### 3.2. The investigation of anthracene radical anion for $CO_2$ fixation

We have repeated Tazuke and Ozawa's photocarboxylation experiment using the conventional solvents DMF and acetonitrile. We used DMA as the electron donor, and a continuous flow of $CO_2$ as the $CO_2$ source; however, our experiment used lower reactant concentrations than these authors. In our DMF experiment we also found production of the dihydrocarboxylic acid **I** as product in 11% yield. When acetonitrile was used as the solvent we too found only trace amounts of **I**. The results and reaction conditions are

Table 1
Solvent effects on photocarboxylation of anthracene

| Solvent | Photoirradiation (366 nm) time (h) | Consumption of anthracene (%) | Yield[a] of dihydro-carboxylic acid (%) |
|---|---|---|---|
| Acetonitrile[b] | 5 | 23 | < 1 |
| DMF[b] | 5 | 63 | 11 |
| Supercritical $CO_2$[c] | 5 | 87.3 | 34.5 |
| Supercritical $CO_2$[c] | 3 | 88.1 | 32.0 |

[a] 10% estimated confidence level.
[b] In $CO_2$ saturated solvents, [ArH] = 0.001 M, [DMA] = 0.1 M, room temperature.
[c] $T$ = 35.0 ($\pm$0.2)°C, pressure = 1700 ($\pm$20) psi, [Cyclohexane] = 0.01 M, [DMA] = 0.01 M, [ArH] = $1.0 \times 10^{-4}$ M.

presented in Table 1. Examination of Table 1 demonstrates that even after 5 h of photolysis only 23% of the anthracene was consumed in acetonitrile, and 63% of the anthracene was consumed using DMF as solvent. These observations have several distinctive mechanistic implications. The first is the obvious need for a good hydrogen atom donor. The second is that carboxylate anion radical formation (see Scheme 1) may be reversible, either thermally or photochemically. And the third is the possibility that $A^{\cdot-}$ and $D^{\cdot+}$ may diffusively encounter to regenerate A and D. It should also be noted that there is a distinct possibility that carboxylate radical anion could be produced from the encounter complex (or caged radical ion pair). We have not included this possibility in Scheme 1 for the sake of simplicity. In the conventional solvent experiments the concentration of $CO_2$ is the limiting factor, e.g. the concentration of $CO_2$ in DMF was only 0.17 M. To overcome this limitation we have used SC $CO_2$ as the reaction medium. This should greatly enhance the interception of $A^{\cdot-}$, and in the presence of a suitable hydrogen donor, should produce a substantially higher yield of carboxylic acid as product.

As with the conventional solvents, our first SC $CO_2$ experiments were performed using 5 h of 366-nm irra-

diation. However, subsequent experiments demonstrated that 3 or even 2 h irradiation gave comparable results (see Tables 1 and 2). Considerably lower concentrations of reactants were used in the SC $CO_2$ experiments (anthracene = $1 \times 10^{-4}$ M; DMA = 0.01 M) to insure complete solubility of reactants and that photolysis was performed under homogeneous reaction conditions. This was visually verified using the high pressure optical cell. The SC $CO_2$ experiments also required a hydrogen donor to produce the carboxylic acid. In the first series of experiments, cyclohexane was used as R–H and the experiments were performed at 35°C and a moderate pressure of 1700 psi. (The critical temperature and pressure of pure $CO_2$ are 31°C and 1070 psi, respectively.) As predicted, under these SC $CO_2$ reaction conditions the yield of dihydrocarboxylic acid **1** was significantly increased to 34.5 and 32% for two consecutive runs (see Table 1). HPLC analysis indicated that the only other detectable compounds following photoirradiation were the radical ion pair coupling product **II**, [see Eq. (4)], and un-reacted anthracene and DMA.

The influence of pressure on the photocarboxylation reaction was investigated in the next series of experiments. Experiments were performed at 1200, 1700,
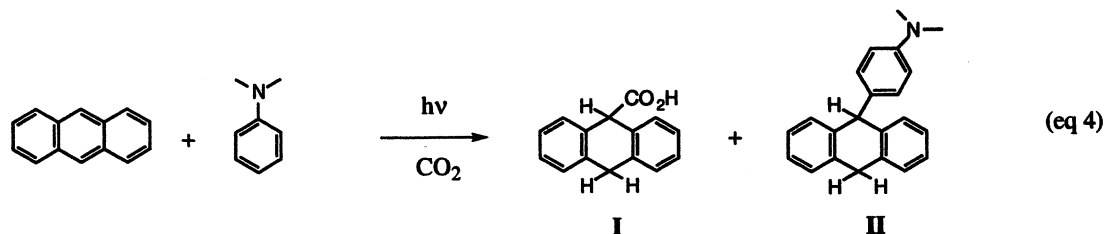


(eq 4)



(eq 5)

Table 2
$CO_2$ pressure dependence of anthracene photocarboxylation

| Pressure of $CO_2$ (psi) | Photoirradiation (366 nm) time (h) | Consumption of anthracene (%) | Yield[a] of dihydro-carboxylic acid (%) |
|---|---|---|---|
| 1200 | 2 | 84.0 | 31.3 |
| 1700 | 2 | 86.0 | 32.0 |
| 2500 | 2 | 88.0 | 37.0 |
| 3500 | 2 | 87.0 | 47.0 |

[a] 10% estimated confidence level; [ArH] = [Anthracene] = $1.0 \times 10^{-4}$ M, [Cyclohexane] = 0.01 M, [DMA] = 0.01 M.

2500 and 3500 psi, while all other experimental parameters were unchanged. Clearly, these experiments demonstrate a consistent increase in the yield of **1** with an increase in reaction pressure (see Table 2). This increase in yield is most likely due to the higher concentration of $CO_2$ at higher pressures, rather than a true thermodynamic pressure effect on the reaction rate constants. Thermodynamic pressure effects on reaction rate constants have been reported to be minimal for a similar electron transfer reaction that produced an aromatic radical anion (Takahashi and Jonah, 1997) and for hydrogen atom abstraction reactions in supercritical fluids (Roberts et al., 1995). At higher SC $CO_2$ pressure, $CO_2$ density is significantly greater and therefore $CO_2$ is more competitive in trapping $A^{\cdot-}$ compared with the alternative deactivation pathways of $A^{\cdot-}$. This enhanced competition is clearly reflected in Tables 1 and 2 by comparing the percent consumption of anthracene in the conventional solvents used to that observed in SC $CO_2$. Although, the hydrogen donating ability of cyclohexane compared to acetonitrile and DMF will also be reflected in that comparison.

The next series of experiments were designed to test the influence of changing the nature of the hydrogen donor on the photocarboxylation reaction. These experiments were each performed at 35°C and 2000 psi with, otherwise, the same constant reaction conditions as previously described. For the reaction outlined in Eq. (4) and detailed in Scheme 1, it can be seen that the hydrogen donor may have to act as both a hydrogen atom source and as a proton source. Unlike acetoni-

trile, cyclohexane is a fairly good hydrogen atom donor, however a poor proton donor. With the later limitation in mind, it was encouraging to observe such significant yields of **1** (up to 47%, Table 2) when cyclohexane was used as the hydrogen source. To test the influence of the hydrogen atom donating ability of the hydrogen source 1,4-cyclohexadiene (1,4-CHD) was used. 1,4-CHD is known as a good hydrogen atom donor, since abstraction produces a resonance stabilized radical product. Using 1,4-CHD the yield of **1** increased substantially to 56.2%, cyclohexane was 30.8% at comparable conditions (see Table 3). 2-Propanol was also investigated since it is a fairly good hydrogen atom donor, as well as a potential proton source. Yield of **1** increased to 57.0%. It is interesting to compare the hydrogen atom and proton donating ability of the three hydrogen sources used in these experiments. Although they may not truly represent hydrogen atom abstraction ability, we can compare our results with the hydrogen-carbon (H–C) bond strengths ($D_{298}^0$/kJ mol$^{-1}$) in question. $D_{298}^0$/kJ mol$^{-1}$ have been calculated from enthalpies of formation for H-cyclohexyl, H-cyclohexa-1,4-dien-3-yl and H-$C(CH_3)_2OH$ and the values are reported (Lide, 2000) to be 399.6 ($\pm 4$), 305.4 ($\pm 8.4$) and 381($\pm 4$) kJ mol$^{-1}$, respectively. As expected, the $D_{298}^0$ values indicate that 2-propanol is a better hydrogen atom donor than cyclohexane, and this is reflected in the corresponding product yields. However, 1,4-CHD seems to be an outlier. Two factors must be considered in this crude analysis. First, the $D_{298}^0$ calculation does not take into consideration the fact that hydrogen atom abstrac-

Table 3
The influence of various hydrogen donors on anthracene photocarboxylation

| H-donor | Photoirradiation (366 nm) time (h) | Consumption of anthracene (%) | Yield[a] of dihydro-carboxylic acid (%) |
|---|---|---|---|
| Cyclohexane | 2 | 88.1 | 30.8 |
| 1,4-Cyclohexadiene | 2 | > 99 | 56.2 |
| 2-Propanol | 2 | > 99 | 57.0 |

[a] 10% estimated confidence level, [ArH] = [Anthracene] = $1.0 \times 10^{-4}$ M, [H-donor] = 0.01 M, [DMA] = 0.01 M, $T = 35.0$ ($\pm 0.2$)°C, pressure = 2000 ($\pm 20$) psi.

tion from 1,4-CHD produces a doubly allylic cation that has considerable resonance stabilization, which makes 1,4-CHD an excellent H-atom source. Secondly, when considering the overall importance of these H-donors, 2-propanol also has significant proton donating ability. Furthermore, once 2-propanol has undergone H-atom abstraction, a ketyl radical is produced. As pointed out by a reviewer, it turns out that ketyl radical is an even better proton source than 2-propanol, processing a $pK_a \sim 10$ (in water). The carboxylic acid yields indicate that 1,4-CHD and 2-propanol are nearly equivalent as overall H-donors and this is most likely due to these individual factors. As for the ability of the hydrogen source to donate a proton, the hydrocarbons seem to be unlikely sources having typical $pK_a$ values in the high 30 to $> 40$ range. The $pK_a$ of 2-propanol is 16.5. It should be noted that other potential proton sources exist in the reaction system. They are: DMA, which has a $pK_a$ of 5.12, and water. There is the possibility that trace amounts of water were present in the reaction mixtures, which would subsequently produce carbonic acid. From the values of $D_{298}^0$ and $pK_a$ presented above it seems reasonable that the mechanism of carboxylic acid formation proceeds first by fairly rapid hydrogen atom abstraction followed by protonation of the remaining carbanion using the most available proton source.
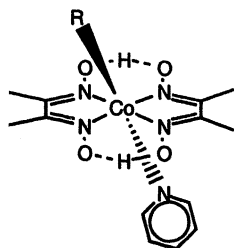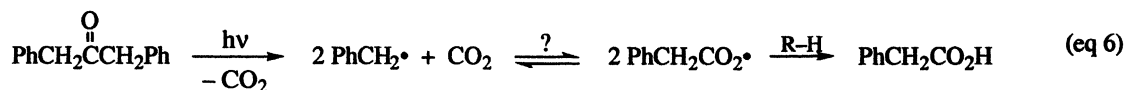
### 3.3. The investigation of carbon-centered free radicals for CO₂ fixation

As mentioned in Section 1, carbon-centered free radicals are potential reactive intermediates for $CO_2$ fixation. A carbon-centered free radical could add to $CO_2$ to produce a carbonyloxyl radical, as described in Eq. (5). If this is an equilibrium process, then in SC $CO_2$, the equilibrium could favor the carbonyloxyl radi-
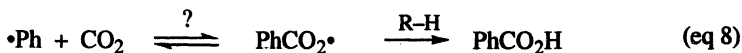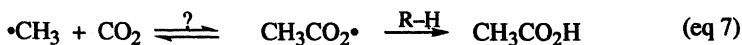
cal. Then in the presence of sufficient amounts of hydrogen atom donor, carboxylic acid could be formed. We have examined this possibility by photolytic generation of three different carbon centered free radicals in SC $CO_2$ in the presence of R−H. First, we generated benzyl radical ($PhCH_2^{\cdot}$) by photolysis of dibenzylketone [see Eq. (6)], a known benzyl radical source (Roberts et al., 1993), in the presence of the same concentrations of hydrogen atom donor (cyclohexane) that we used in the radical anion experiments. No benzylcarboxylic acid was detected by HPLC analysis using authentic $PhCH_2CO_2H$ as a reference. This result was not surprising since previous laser flash photolytic generation of $PhCH_2^{\cdot}$ in pure SC $CO_2$ demonstrated that $PhCH_2^{\cdot}$ decayed with pure second-order kinetics (Roberts et al., 1993). That is, $PhCH_2^{\cdot}$ does not react with SC $CO_2$ but decays by means of ($PhCH_2^{\cdot}/PhCH_2^{\cdot}$) radical−radical termination.

$$R^{\cdot} + CO_2 \overset{?}{\rightleftharpoons} R\text{-}CO_2^{\cdot} \overset{R\text{-}H}{\rightarrow} R\text{-}CO_2H \qquad (5)$$
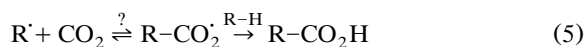
Our next series of experiments generated the more reactive methyl and phenyl radicals from the corresponding alkylcolbaloximes [Eqs. (7) and (8)] which are known photolabile precursors of methyl and phenyl radicals (Schrauzer, 1967; Bakac and Espenson, 1987; Endicott et al., 1989). Again, when using these radical sources, R−H was added in comparable concentrations as in the radical anion carboxylation experiments. Following irradiation, HPLC analysis detected no acetic acid or benzoic acid as product. Therefore, even if methyl and phenyl radicals react with SC $CO_2$ to produce $RCO_2^{\cdot}$ the lifetime of $RCO_2^{\cdot}$ is not long enough to be trapped by the hydrogen atom donor, at least under the same conditions that successfully trapped the anthracene radical ion.



$$PhCH_2\overset{O}{\overset{\|}{C}}CH_2Ph \overset{h\nu}{\underset{-CO_2}{\longrightarrow}} 2\ PhCH_2{\cdot} + CO_2 \overset{?}{\rightleftharpoons} 2\ PhCH_2CO_2{\cdot} \overset{R\text{-}H}{\longrightarrow} PhCH_2CO_2H \qquad (eq\ 6)$$

$${\cdot}CH_3 + CO_2 \overset{?}{\rightleftharpoons} CH_3CO_2{\cdot} \overset{R\text{-}H}{\longrightarrow} CH_3CO_2H \qquad (eq\ 7)$$

$${\cdot}Ph + CO_2 \overset{?}{\rightleftharpoons} PhCO_2{\cdot} \overset{R\text{-}H}{\longrightarrow} PhCO_2H \qquad (eq\ 8)$$

R = CH₃; Ph

## 4. Conclusions

We have demonstrated that it is possible to generate an aromatic radical anion via a photoinduced electron transfer mechanism in SC $CO_2$. It is also possible to trap the aromatic radical anion with appropriate hydrogen donors (cyclohexane, 1,4-CHD and 2-propanol) to produce a carboxylic acid product, i.e. $CO_2$ fixation. Therefore, SC $CO_2$ can be effectively used as both an environmentally benign solvent and act as an environmentally friendly $C_1$ feedstock. Alternatively, under comparable conditions, carbon-centered free radicals do not produce carboxylic acid products. Finally, we would like to recognize a reviewers comment that, due to the use of our high energy photo-source (1000 W Xe lamp) and our rather long photolysis times, these experiments would most likely produce more $CO_2$ (from the energy requirements of the experiment) than would be consumed in the $CO_2$ fixation reactions. Of course, this would be environmentally undesirable. This problem most certainly could be overcome by the substitution of the white light source, which produces a full spectrum of mostly unused photons, with a more efficient laser source. By the use of high photo-flux monochromatic laser light, of which several suitable wavelength specific laser types are available, photoexcitation times may be reduced to minutes and in turn reduce overall energy requirements. An additional valuable improvement designed to enhance efficiency of these experiments would be the development of a non-sacrificial catalyst.

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