Charged Species in the Radiolysis of Supercritical CO_2[†]

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The pulse radiolysis technique has been employed in studying charge-transfer reactions of anionic $C_2O_4^-$, and cationic $C_2O_4^+$ species in supercritical carbon dioxide ($scCO_2$) over a range of reduced densities $\rho_r = 0.36-1.5$ and at a reduced temperature of $T_r = 1.03$. The absorption spectrum measured in the visible region with a maximum around 700 nm is assigned to the dimer cation $C_2O_4^+$. The pressure dependence of charge-transfer reactions was examined using dimethylaniline (DMA), benzoquinone (BQ), and oxygen as charge acceptors. The reaction rates of DMA with cations, and BQ with anions are at or near the diffusion-controlled limit. The rates decrease an order of magnitude with increase of pressure. The reaction of $C_2O_4^+$ with oxygen is much slower with an almost constant rate over the pressure range examined. The measured rate constants of electron-transfer reactions are analyzed in terms of the diffusion constants of reactants in $scCO_2$, and the dependence of measured and theoretical values on the bulk density is discussed.

Introduction

In the past few years there has been considerable effort to study chemical reactions in supercritical fluids, both for scientific and technological reasons. Recently, an issue of *Chemical Reviews* (Vol. 99, no. 2, 1999) was dedicated to the summary of various physicochemical properties, theoretical and computational studies, and chemical reactions in supercritical fluids. The characteristics of chemical reactions in the supercritical fluids arise from inhomogeneity in solute−solvent attractive interaction. The local solvent density of supercritical fluid may be significantly greater than the bulk density of fluid. Unusual microscopic solvation of solutes (sometimes referred to as the clustering of solvent molecules around the solute molecule) in these systems affects the kinetics of energy and charge-transfer reactions.[1−3] Fast techniques of flash photolysis[4,5] and pulse radiolysis[6,7] have been employed to examine both radical and electron-transfer reactions to determine the effects of solvation and solvent reorganization energies.

We recently began studying the formation of radicals and radical ions from the pulse radiolysis of supercritical carbon dioxide ($scCO_2$).[8] The possibility of using $scCO_2$ in reprocessing spent nuclear fuel (UO_2)[9] raises the question of the nature, yields and overall reactions of radiolytically generated species in $scCO_2$. Although there has been considerable previous work on the radiolysis of gaseous and liquid CO_2,[10−14] the reactions of radiolytic products would differ under conditions of supercritical fluids. In addition, pulse radiolysis provides an excellent tool for generating charged species (both positive and negative ions) and examining electron-transfer reactions. In supercritical fluids, fluctuations in solute/solvent homogeneity both in space and time might have a significant effect on reactions, especially charge-transfer reactions.

In this paper, we report on the nature of charged species formed upon pulse radiolysis of $scCO_2$ and their reactions with substrates over a wide range of pressures from 64 to 120 bar at the constant temperature of 40.1 °C (a reduced temperature of $T_r = 1.03$). This range of pressures results in significant changes in fluid density, dielectric constant, and viscosity of $scCO_2$, all of which influence charge-transfer reactions and thus chemical reactivity.

Experimental Section

Materials. All chemicals were of the highest purity commercially available and were used as purchased. The CO_2 was SFC grade-diptube and was purchased from Scott Specialty Gases. The gas passed through a dry ice trap to remove a trace amount of water.

Methods. Experiments were performed in a stainless steel high-pressure cell. Two Suprasil windows (1 cm thick) were mounted to the cell using Teflon O-rings. The cell has an optical path of 5 cm and effective diameter of 1.2 cm. All experiments were done at constant temperature of 40.1 ± 0.1 °C (a reduced temperature of 1.03) as monitored with a temperature controller (Omega, model CN 1001RTD). Pressure in the cell was adjusted using a HPLC (JASCO, model PU-980) pump and monitored with a Cole-Parmer digital pressure meter (model 7350-38). The experimental arrangements were similar to those described previously.[7,8]

Pulse radiolysis experiments were performed at the Argonne 20 MeV linear accelerator with electron pulses of 30 ps or 4 ns. For optical detection, both a monochromator (PTI, model 102) and photomultiplier (Hamamatsu R928) for wavelengths below 450 nm and interference filters (bandwidth 10 or 40 nm) and silicon photodiode (EG&G, FND 100) for longer wavelengths (450 to 1000 nm) were used. The electron pulses were collinear with the analyzing light beam, but in the opposite direction. Dose in the cell was measured using aerated solutions of thiocyanate[15,16] and ferrocyanide.[16] The radiation distribution in the cell was explored by detecting the changes at 320 nm of irradiated Plexiglas (poly(methyl methacrylate)).[17] The plates

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of Plexiglas were calibrated with the Fricke dosimeter.[18] It was found that the dominant effect was the scattering from the front window. Detailed descriptions of the experimental setup and observed dose distribution were published elsewhere.[8] The average dose absorbed in a sample was 7.6ρ Gy and 27.5ρ Gy for 30 ps and 4 ns pulses, respectively, where ρ is the density of $scCO_2$ in g/cm^3. The dose varied by less than 10% from day to day.

Solid samples such as *p*-benzoquinone and *p*-chloranil were dissolved in ether and kept as stock solutions. The desired volume of stock solution was added to the open cell at a temperature of 40.1 °C. After evaporation of the ether, the cell was sealed, evacuated and finally filled with CO_2. When making samples of *N*,*N*-dimethylaniline, the cell was purged with CO_2 gas for approximately 10 min, after which the flow was decreased and *N*,*N*-dimethylaniline was injected into the cell using a syringe. The cell was then immediately closed and pressurized with CO_2. Gaseous additives were added in the evacuated cell to the desired pressure, and then the cell was pressurized with CO_2. Carbon monoxide (AGA, 99.993%) was passed through a liquid nitrogen trap in order to remove impurities.

The kinetic data were analyzed using a nonlinear least-squares fitting routine for optical absorption signals. The PVT relationships of $scCO_2$ were calculated using the BWR eq 19.

Results and Discussion

The radiolysis of gas-phase carbon dioxide has been the subject of many investigations.[10−14] The initial processes as well as charge neutralization and ion−molecule reactions are well-known, and a quantitative numerical model that includes reaction rates and yields has been postulated.[14] The primary process in radiolysis of gaseous carbon dioxide, besides excitation, is ionization of CO_2 to give electrons and positive ions CO_2^+ (and/or fragmented ions of CO_2^+: CO^+, C^+, O^+, although with much lower yields). Similarly, the ionization of $scCO_2$ will result in the formation of the electrons and CO_2^+ ions as primary species. However, their distribution and subsequent fate will be different from that in the gas phase.

Anionic Species, Reduction of Benzoquinone. It is known that CO_2 is an efficient electron scavenger in liquids[20] and a poor one in low-pressure gases.[21] The lifetime of electron bound to CO_2 molecule might be less than 10^{-15} s due to autoionization/autodetachment,[22] as long as it retains the linear equilibrium geometry.[23] On the other hand, supersonic beam experiments have shown an efficient attachment of an electron to carbon dioxide clusters, resulting in the relatively long-lived cluster anions $(CO_2)_n^-$ ($n \geq 2$).[22−26] It is shown that energetically the most stable structure of dimer $(CO_2)_2^-$ corresponds to the bent CO_2^- anion solvated by nearly a linear CO_2.[23,27] We have tried to observe absorption spectra of negative species in neat $scCO_2$, but we were unable to detect any transient absorption that could be attributed to anions in the range of 250−1000 nm. Instead, to examine the formation and reactions of negative cluster species $(CO_2)_n^-$ upon pulse radiolysis of $scCO_2$, we probed the reduction of *p*-benzoquinone (BQ).

$$(CO_2)_n^- + BQ \rightarrow BQ^- + nCO_2 \qquad (1)$$

The relatively high solubility of BQ in $scCO_2$ (range of millimolar concentrations) and its high electron affinity ($E° = -0.54$ V vs SCE) enable electron-transfer reaction 1 to occur. In Figure 1, the absorption spectrum recorded 60 ns after an electron pulse in a solution of 0.2 mM BQ in 78 bar $scCO_2$ is presented. The spectrum is given in $G\epsilon$ units, where G is the radiation chemical yield (number of molecules per 100 eV absorbed energy) and ϵ is the extinction coefficient in M^{-1} cm^{-1}. The absorption was corrected for the contribution from Suprasil window absorption. The spectrum corresponds well to the benzoquinone anion radical (BQ^-) previously reported.[28−30] When 1 bar of sulfur hexafluoride was added into the system, no absorption due to BQ^- was observed. The SF_6 scavenges both anions and thermal electrons, which are precursors of carbon dioxide anion clusters.[11] Therefore, the observed spectrum is a result of electron-transfer reaction from anionic species (presumably $(CO_2)_n^-$) to BQ.

Both the yield and the rate of BQ^- formation depend on the pressure of CO_2. An inset of Figure 1 demonstrates how the density of the supercritical fluid alters the kinetics of charge-transfer reactions. The rate constant of reaction 1 was determined as a function of pressure of CO_2 by measuring the pseudo-first-order rate as a function of the concentration of BQ from 0.2 to 1.2 mM. An example of the optical absorption signals observed at 320 nm for different concentrations of BQ is presented in Figure 2a. The rate of formation of benzoquinone anion depended linearly on BQ concentration for all pressures from 63 to 120 bar (see an example in Figure 2b.). Nonlinear least-squares fitting was applied to fit the pseudo-first-order growth and decay of the BQ^- transient absorption signals. Values determined for the rate constants are presented in Table 1. The BQ^- decays within a few microseconds. The transient absorption of an intermediate product in BQ^- decay with an absorption in the UV and a tail toward the visible region is also presented in Figure 1. We were unable to identify the final reaction products because the relevant optical spectra are not known. Possible routes for disappearance of the radical anion BQ^- may involve reactions with cationic species, dimerization,[29] or carboxylation which is known to occur in carbon dioxide.[31] The second-order rate constants of the charge-transfer reaction decrease with increased pressure (density) of $scCO_2$, as shown in Figure 2c. That the yields of BQ^- are affected by kinetics parameters and not by the differences in the energy deposited by ionizing radiation is demonstrated in Figure 2c, where maximum values of optical densities of BQ^- are normalized to the unit density. The energy deposited by ionizing radiation in the sample, and thus concentration of radicals, depends on the density. The ionization events are well separated over the entire density range and do not affect the kinetics of charge-transfer reaction 1. Therefore, only the changes in bulk density of supercritical carbon dioxide influence the rate of BQ^- formation. Details of the kinetics will be discussed later.

Though we observed electron-transfer to BQ, it is not clear what type of cluster anions $(CO_2)_n^-$ are the electron donors. In the gas-phase cluster experiments, negatively charged clusters of carbon dioxide have been observed by low-energy electron attachment to the neutral clusters. The negative ion cluster size distribution was found to be electron energy dependent.[24,32] The larger clusters ($n > 4$) are formed with near zero energy electrons, while the smaller clusters such as dimers are only produced above a threshold energy of about 1.5 eV. In radiolysis experiments, ions, radicals, and secondary electrons are created by the interaction of the high-energy ionizing particle with the electrons of the molecules in the system. There is considerable energy in the exciting secondary electron (10−100 eV). This electron can then go a considerable distance in the solution before it loses all of its energy and is thermalized. After an electron has lost its excess energy, its motion is diffusive. The thermalized electron can attach to a neutral cluster and form a

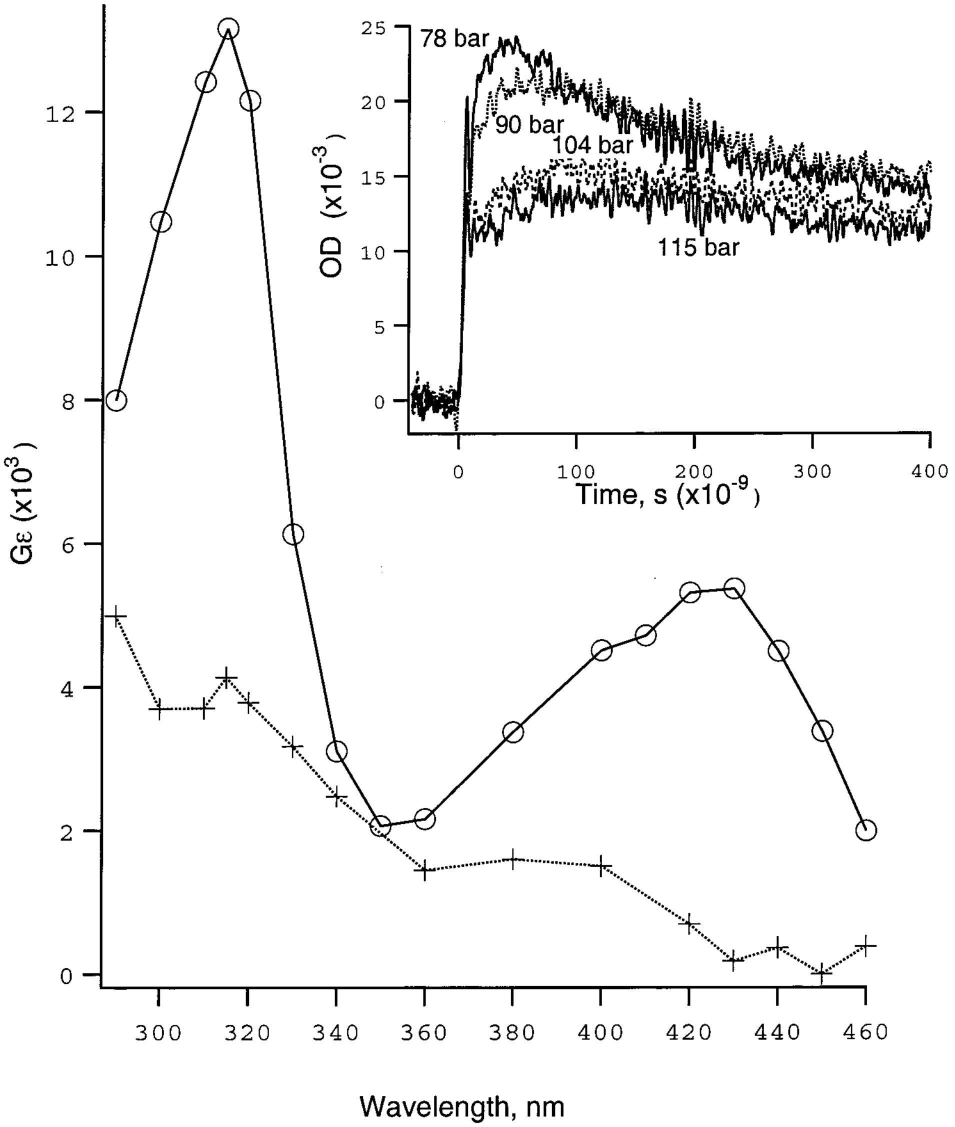

Figure 1. Absorption spectra in Gϵ units observed (○) 60 ns and (+) 7.7 μs after the electron pulse in solution of 0.2 mM benzoquinone in 78 bar CO_2. Dose 2.1 Gy per pulse. Inset: transient signals detected at 320 nm of 0.2 mM solutions of BQ at different pressures of CO_2.

cluster anion. It is known that CO_2 molecules form neutral clusters under supercritical conditions.[3] It is also known that CO_2 neutral clusters exhibit a wide size distribution, and the distribution changes with pressure and temperature. Therefore, in scCO_2 a wide range of cluster anions could occur. If one considers a fast reaction kinetics observed in electron transfer and a slow diffusivity of larger clusters, it is likely that at least at low pressures the major donor of electrons is a small cluster like a dimer $(CO_2)_2^-$.

We intended to study the rates of the electron-transfer reaction from the solvent anion to a series of solutes as a function of the redox potential of the solute. The low solubilities of many electron scavengers in scCO_2, coupled with the short lifetime of the CO_2 anion, limited the number of systems that we could study. We attempted to study the reduction of *p*-chloranil (Ch), but the experimental results were not straightforward. Specifically, the formation of chloranil anion radical (Ch^-) was complicated by excitation of chloranil molecules. The Ch^- anions were formed during the rise time of our detection system (3−4 ns), too fast to be a result of electron-transfer reaction 1, even though chloranil has very high electron affinity ($E° = -0.02$ V vs SCE). Addition of SF_6 revealed a superposition of optical signals of different transient species. The spectrum recorded at 30 ns after the pulse is presented in Figure 3. Although not resolved completely, the spectrum resembles that of a Ch^- anion radical in MTHF and DMSO solvents,[33] with a somewhat broader peak at 450 nm. The generation of a singlet excited state of chloranil as a result of some ion-neutralization reaction gives a possible explanation for the fast formation of Ch^- anion. It has been shown that both singlet and triplet chloranil are able to capture electron from solvent, such as acetonitrile.[34,35] By analogy to acetonitrile solvent, the oxidation of CO_2 may occur, although the ionization potential of gas-phase CO_2 (13.77 eV) is larger compared to acetonitrile (12.2 eV). Other possibilities include deactivation of excited states to give both chloranil cations and anions. We have not studied the possible reactions in detail because they were beyond the scope of this work.

Cationic Species, $C_2O_4^+$. In contrast to the anionic species, we have been able to observe the absorption spectrum of the cationic species and have assigned it to the $C_2O_4^+$ cation. In Figure 4, the absorption spectrum of $C_2O_4^+$ cation measured within 10 ns after the electron pulse in neat scCO_2 is presented together with the photodissociation spectrum observed previously in the gas-phase cluster experiments.[36] The photodissociation spectrum of cationic species decreases sharply at longer

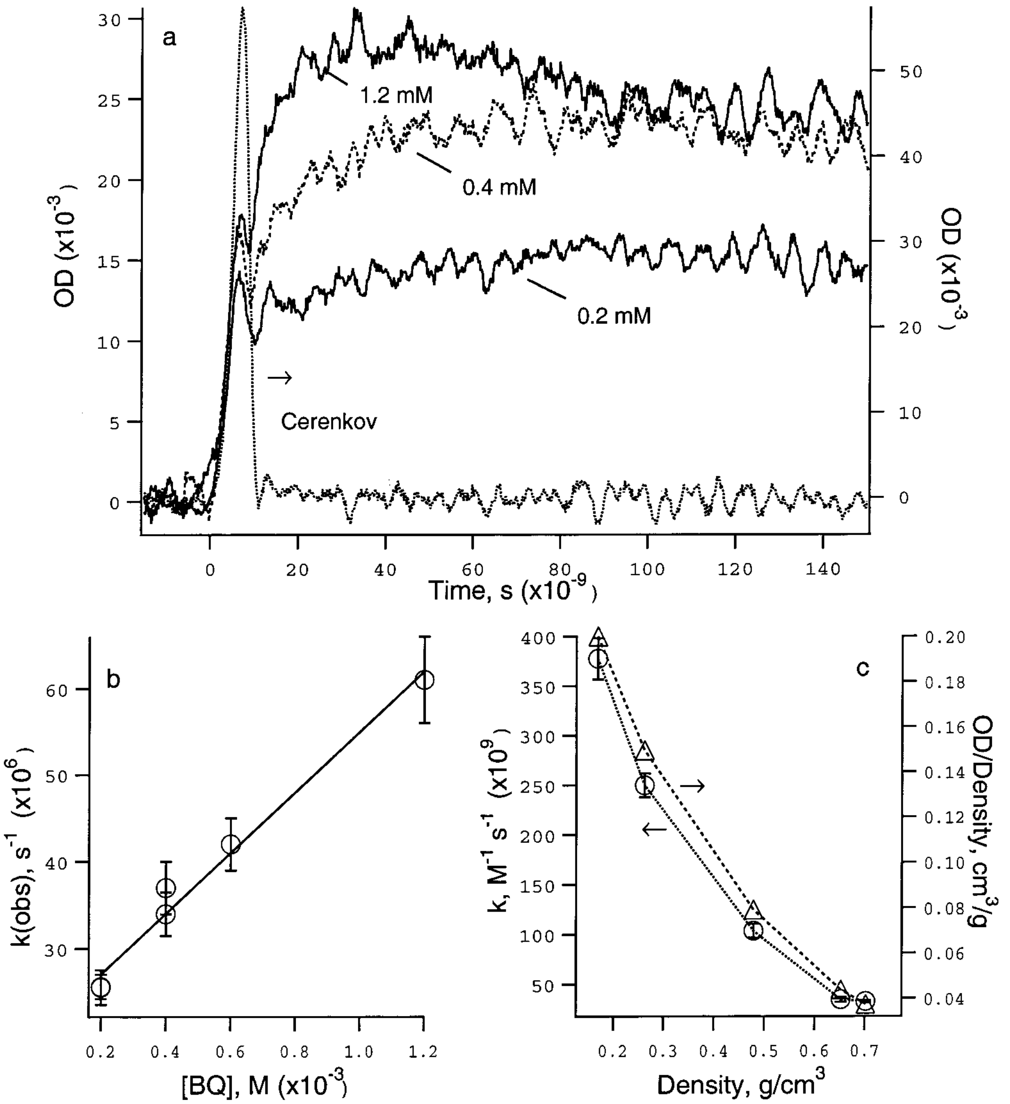

Figure 2. (a) Difference transient signals detected at 320 nm in solutions containing 0.2, 0.4, and 1.2 mM benzoquinone. All solutions are at 104 bar CO_2. The step at approximately 5 ns is due to Cerenkov light and arises from the data treatment technique used. The Cerenkov signal from independent experiment is also presented. (b) Pseudo-first-order rate of formation of BQ^- at 104 bar CO_2. (c) Rate constants of the reaction between anion and BQ (○), and normalized yield of BQ^- (△) as a function of density of $scCO_2$.

TABLE 1: Rate Constants for the Electron-Transfer Reactions with Ionic Species

density (g/cm³)	k_{BQ} 10^{11} (M^{-1} s^{-1})[a]	k_{DMA} 10^{11} (M^{-1} s^{-1})[b]	k_{oxygen} 10^{10} (M^{-1} s^{-1})[c]
0.168	3.8 ± 0.2	4.18 ± 0.02	6.7 ± 1.3
0.284	2.5 ± 0.1	3.5 ± 0.2	8.7 ± 0.2
0.478	1.0 ± 0.1	2.2 ± 0.02	6.0 ± 0.5
0.653	0.35 ± 0.03	1.2 ± 0.01	4.4 ± 0.2
0.707	0.34 ± 0.01	0.83 ± 0.03	4.4 ± 0.4

[a] Rate constants for reaction 1. [b] Rate constants for reaction 2. [c] Rate constants for reaction 3.

wavelengths compared to the absorption spectrum. This is not surprising as quantum efficiency for photodissociation might well be expected to decrease at low photon energies. The transient species absorbing in the visible does not react with electron scavengers, such as SF_6 and BQ, while it reacts with electron donors. This further confirmed the identity of $C_2O_4^+$ cation. The amount of $C_2O_4^+$ cation formed was not proportional to the density of $scCO_2$ (see Figure 4c). In our previous paper,[8] we discussed in detail the influence of the geminate recombination of electrons with positive ions (probably CO_2^+, as precursors for $C_2O_4^+$) and their escape probability given by the Onsager relationship, in terms of possible scattering of electrons. We have shown that the general shape as observed in Figure 4c can be expected.[8]

The transfer of electrons from *N*,*N*-dimethylaniline (DMA), reaction 2, and oxygen, reaction 3, to $C_2O_4^+$ cations was examined by following the decay of the optical absorption of the cationic species at 700 nm. The kinetics were pseudo-first-order over the range of the concentration examined (0.3−1.6 mM for DMA and 0.5−3.6 mM for O_2).

$$C_2O_4^+ + DMA \rightarrow DMA^+ + 2CO_2 \qquad (2)$$

$$C_2O_4^+ + O_2 \rightarrow O_2^+ + 2CO_2 \qquad (3)$$

In Figure 5, the changes in absorption signals of $C_2O_4^+$ with the addition of oxygen are presented. The inset illustrates the linear dependence of the rates on the concentration, which was observed throughout the whole range of densities, both for oxygen and DMA. The measured rate constants for reactions 2 and 3 are listed in Table 1, and their dependence on density of CO_2 will be discussed below. In the case of dimethylaniline, the product of reaction 2 was detected at 460 nm, where DMA^+

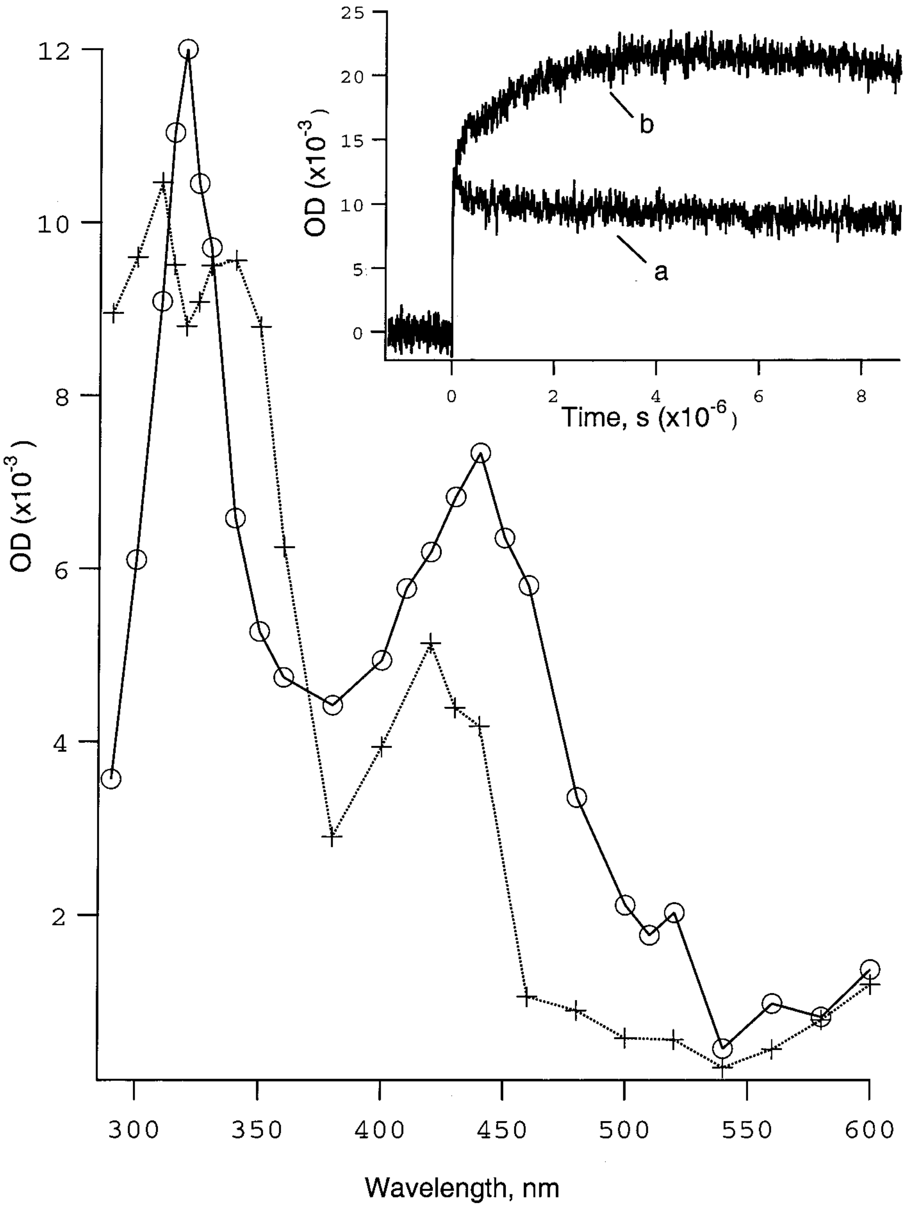

Figure 3. Difference transient spectra observed (○) 30 ns and (+) 4.7 μs after the electron pulse in solution of 0.1 mM chloranil at 104 bar CO_2. Dose 5 Gy per pulse. Inset: transient signals detected at 320 nm in the absence (a) and in the presence (b) of SF_6. Dose 18 Gy per pulse.

cation absorbs.[37] Interference from the DMA triplet absorption, whose spectrum is very close to that of the cation, prevented resolution of the signal growth at 460 nm.

We have found that carbon monoxide also reacts with $C_2O_4^+$ cations by observing the decay of the 700 nm absorption upon the addition of CO. In gaseous CO_2, the following reactions have been proposed:[14]

$$C_2O_4^+ + CO \rightarrow C_2O_3^+ + CO_2 \quad (4)$$

$$C_2O_3^+ + CO \rightarrow C_2O_2^+ + CO_2 \quad (5)$$

$$C_2O_2^+ + CO \rightarrow CO^+ + 2CO \quad (6)$$

Our experiments have shown that the dependence of the rate of reaction with CO was not linear with the carbon monoxide concentration (see Figure 5, inset). This suggests a complex mechanism similar to the one postulated for the gas phase, or some additional bimolecular process. We had no means to reveal such a complex mechanism other than to look for the absorption of possible cations ($C_2O_3^+$, $C_2O_2^+$, or CO^+) and could not detect any residual absorption at the end of the reaction of $C_2O_4^+$ with CO. The photodissociation spectrum of $C_2O_2^+$ ion has a maximum around 460 nm, but the cross section is 2 orders of magnitude less than for $C_2O_4^+$ cation.[36] At present, we cannot distinguish between possible reactions of cations with CO in $scCO_2$. Further investigations on the reactions of CO in $scCO_2$ are required.

Reaction Kinetics. The rate of electron-transfer reactions between anions with benzoquinone and cations with dimethylaniline decreased with the density of $scCO_2$ (see Table 1). The observed rate constants on the order of 10^{11} M^{-1} s^{-1} are typical for diffusion-controlled reactions in supercritical fluids. Diffusion-controlled reactions in supercritical fluids fall between two limiting conditions, that of the liquid and of the gas phase. In low-pressure gases, the diffusion-controlled limit is independent of density and equals the collision rate constant given by the kinetic theory of gases. In liquid solutions, the rates can be modeled effectively with the Smoluchowski equation. Between these two limiting conditions, which can be clearly distinguished when rates are presented as a function of inverse reduced

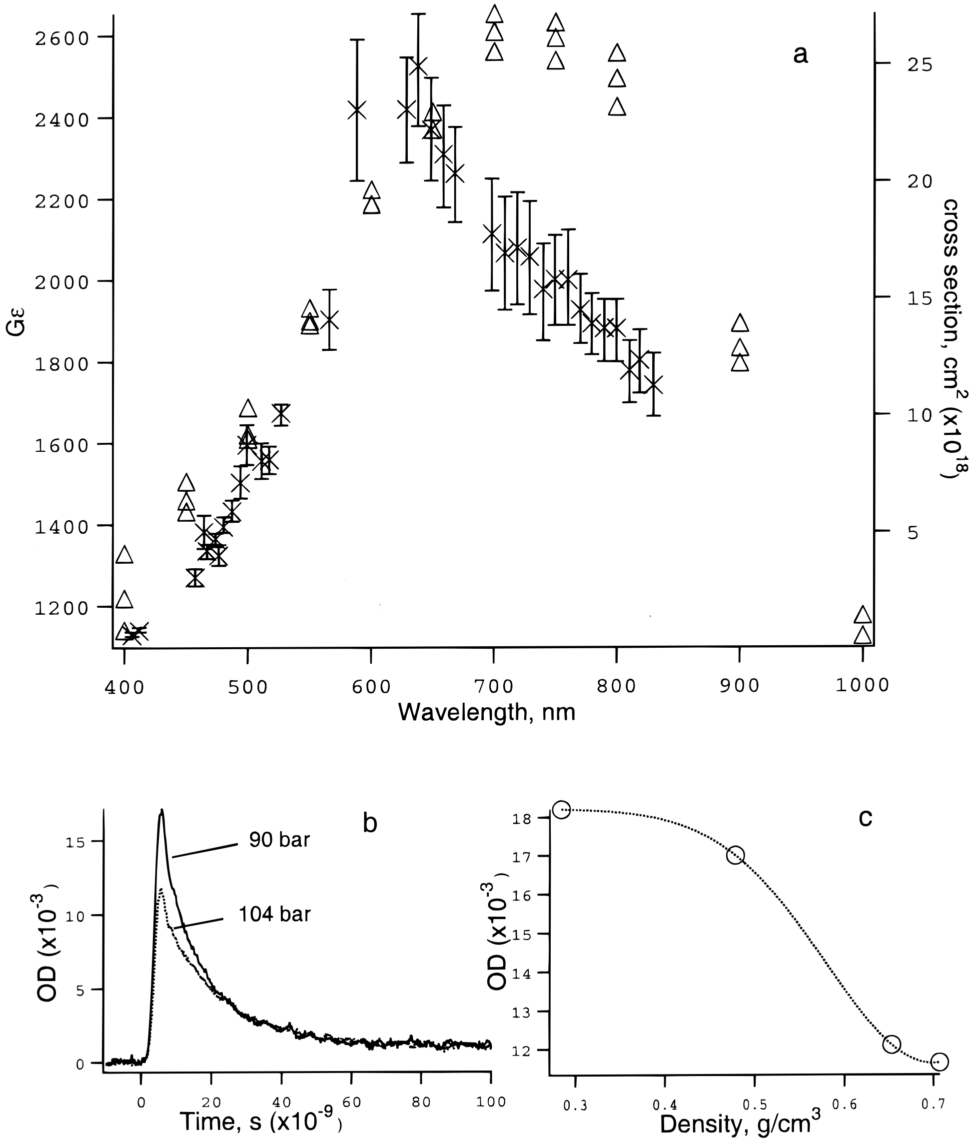

Figure 4. (a) Absorption spectrum in Gϵ units of $C_2O_4^+$ observed 10 ns after the electron pulse in neat $scCO_2$ at 104 bar ($\triangle$). Dose 18 Gy per pulse. The photodissociation spectrum from ref 36 is also presented ($\times$). (b) Difference transient signals detected at 700 nm for 90 and 104 bar CO_2. (c) Changes in the yield of $C_2O_4^+$ cation absorption with density of $scCO_2$.

density,[38] lay the values for diffusion-controlled reactions in supercritical fluids. The small changes in pressure in the near-critical region make significant changes in the solvent viscosity, and thus, the rate of reactions.

To estimate the upper limit of the rate of barrierless reactions in supercritical fluids, one can apply the Stokes−Einstein law, eq 7,

$$k_{\mathrm{diff}} = 8k_{\mathrm{B}}T/3\eta \tag{7}$$

where η is viscosity of fluid and k_{B} is the Boltzman constant. Alternatively, if diffusion coefficients for both reactive species, D_{A} and D_{B}, are known, one can evaluate the diffusion-controlled rate constant using the Smoluchowski eq 8, where R is reaction distance and N is Avogadro's number.

$$k_{\mathrm{diff}} = 4\pi N(D_{\mathrm{A}} + D_{\mathrm{B}})R \tag{8}$$

In principle, the Smoluchowski equation can be used in calculating the diffusion-controlled rate constants in supercritical fluids. The problem arises in determining accurately the diffusion coefficients of reactants and the reaction distance under such conditions. For $scCO_2$, there are considerable experimental data on diffusion coefficients of specific solutes. Several methods have been proposed to predict or correlate the diffusion coefficients in supercritical fluids resulting in empirical or semiempirical equations.[39,40] The various methods are based on the Stokes−Einstein equation, a hard-sphere model, a free-volume model, or molecular dynamics results for the Lennard-Jones fluids. To estimate infinite dilution diffusion coefficients we used eq 9,[40]

$$D_{21} = (A \times 10^{-9})(V_1^{\,k} - B)(T/M_2)^{1/2} \tag{9}$$

which takes into account CO_2 molar volume V_1 calculated by the BWR equation, temperature T, and molecular mass of solute M_2. The exponent k expresses the dependence on the reduced density, $\rho_{\mathrm{r}} = \rho/\rho_{\mathrm{c}}$, while constants A and B include values for the critical pressure and molar volume of CO_2. The equation has been shown to correlate values within 10% average absolute error for liquid and solid solutes and reduced densities between 0.21 and 2.0.[40] Using this method we estimated diffusion coefficients for BQ and DMA in $scCO_2$, while for the $C_2O_4^+$ and $C_2O_4^-$ ions, diffusion coefficients of the neutral molecules

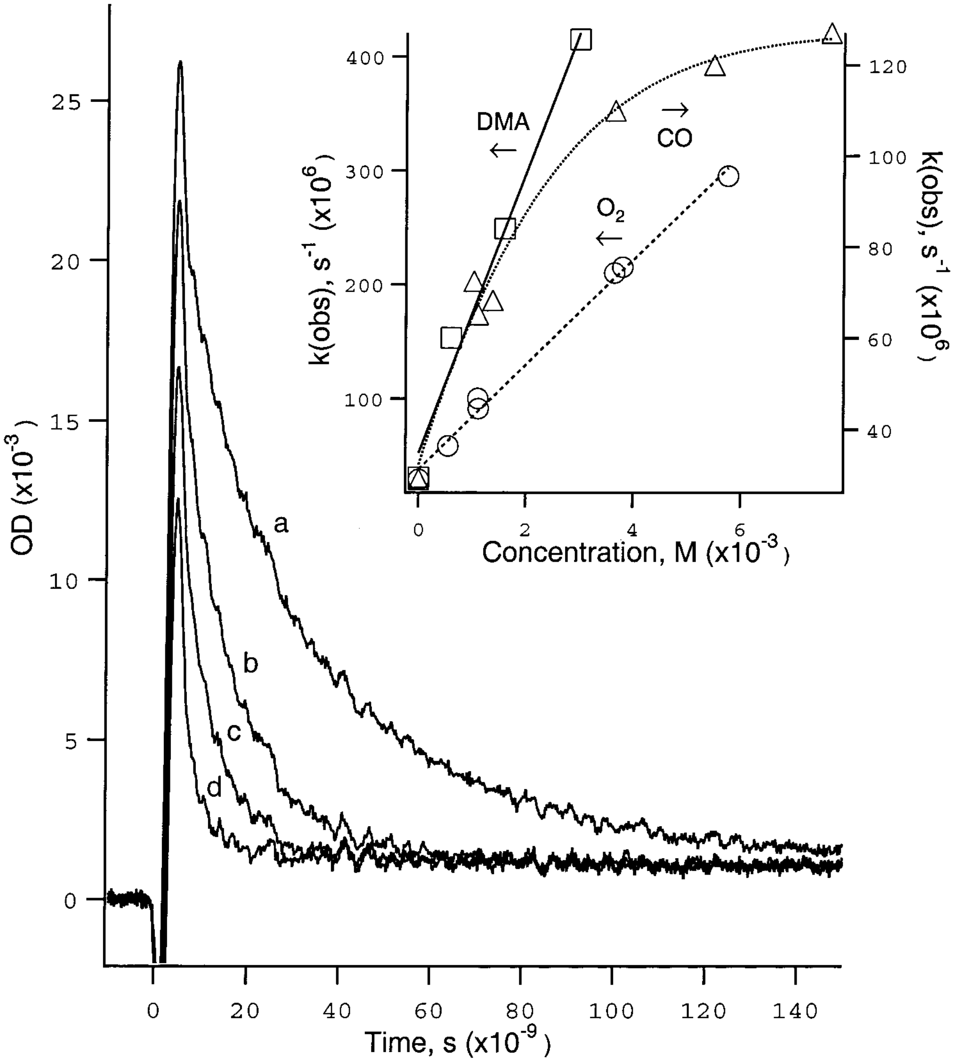

Figure 5. Difference transient signals detected at 700 nm in 80 bar of CO_2 in the presence of oxygen. Concentrations of O_2 are (a) 0, (b) 0.55, (c) 1.11, and (d) 3.65 mM. Dose 2.1 Gy per pulse. Inset: dependence of the rate of decay on concentration of (□) dimethylaniline, (○) O_2, and (△) CO at 104 bar of CO_2.

(C_2O_4) were calculated. As discussed earlier, we do not know the size of a cluster anion. Assuming a dimer anion $(CO_2)_2^-$, we obtain an upper limit for the diffusion-controlled rate constant between anions and BQ, because diffusivity of ions is generally less than that of neutral molecules of the same size.[41] The reaction distance of $R = 6.5$ Å used in calculating diffusion-controlled rate constants was approximated as a sum of the donor and acceptor radii. In Figure 6, both the experimental and calculated values are presented. The correlation between experimental and values calculated using diffusion coefficients is good for reaction of DMA with cations, reaction 1, for reduced densities $\rho_r < 1$, where solvation and local density effects are pronounced. Larger discrepancies are observed for high densities of $scCO_2$ and for the reaction of BQ with anions where calculated values present the very upper limit for diffusion-controlled reactions.

The difference between the predicted and the measured rate constants for the reactions of DMA with $C_2O_4^+$ and BQ with $C_2O_4^-$ can be attributed to either (or both) of two causes, diffusion constants are lower than predicted at higher densities or the reactions are no longer diffusion-controlled at higher densities. The diffusion rate constants were calculated assuming the cation/anion was C_2O_4 and it is not clear how accurate that assumption is, particularly at higher densities. However, at low densities, this assumption cannot be far wrong because the calculated diffusion-controlled rate is in good agreement with the experimental rate. Kimura et al.[42] have shown that a large negative ion, α-naphthoquinone anion, diffuses more slowly than the parent molecule in $scCO_2$, and that the ratio of diffusion constant of the anion to the diffusion constant of neutral molecule is 0.45 at reduced density of 2 and 0.7 at reduced density of 1.2. These results are consistent with our experimental results where the rates show a comparable drop over a similar density range for DMA + $C_2O_4^+$ reaction. A larger drop is seen for the BQ + $C_2O_4^-$ reaction. This could be due to an increased clustering so that the better description of electron donor is $(CO_2)_n^-$ rather than just the dimer. The increased clustering would lead to a lower mobility at higher densities. It has been shown that even in low-pressure gaseous CO_2 (density up to 0.1 g/cm^3) the mobility of cationic and anionic species decreases with increasing density.[25]

Another explanation could be that a $(CO_2)_n^-$ species may be formed that will be more stable than the dimer anion. This alternative explanation assumes that the clustering of solvent molecules around the $(CO_2)_2^-$ makes it better solvated and more stable. The reaction would then become slower because there is less excess energy and the electron-transfer process becomes less probable. A similar effect could also occur for the cations,

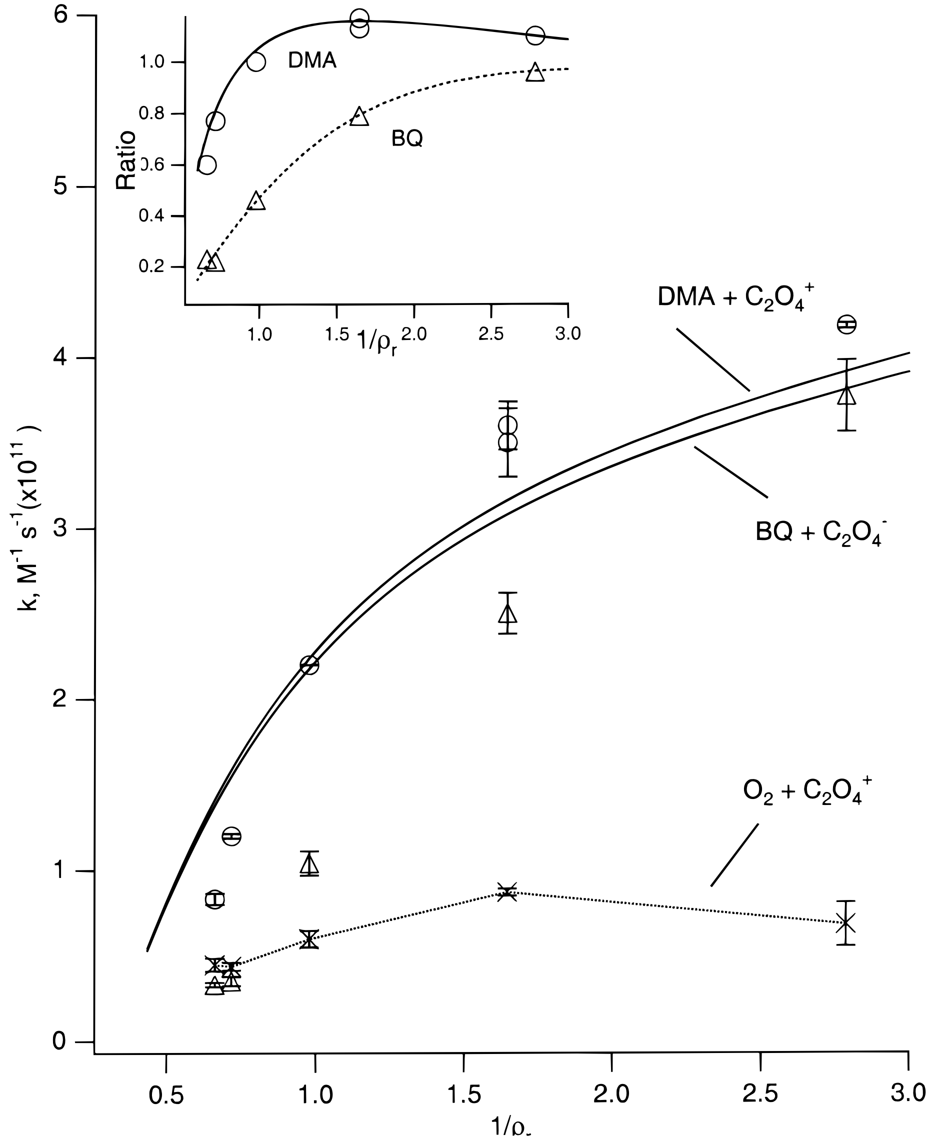

Figure 6. Rate constants for the reaction of (△) $C_2O_4^-$ with benzoquinone and $C_2O_4^+$ with (○) dimethylaniline and (×) oxygen. Dotted lines connect the experimental values. Full lines represent calculated values of rate constants for diffusion-controlled reactions according to eqs 8 and 9. Inset: ratio of the experimental to calculated rate constants.

although such an explanation does not appear to be necessary for the cation reactions because the rates are well explained from the changes in mobility.

At present, it is not possible to distinguish between the different possibilities. Better information on how the diffusivity of charged entities is altered in supercritical fluids will be critical to understanding the fundamental origins of these effects. The use of transient (microwave or dc) conductivity might make it possible to measure cation and anion mobilities as a function of density of $scCO_2$.

The reaction of oxygen with $C_2O_4^+$ is not diffusion-controlled in gas-phase carbon dioxide,[14] and it is well below the diffusion limit in $scCO_2$ over most of the density range we have studied (see Figure 6). Energetically, reaction of $C_2O_4^+$ with O_2 is less favorable than the reaction of cation with DMA because of the difference in O_2 and DMA ionization potentials of about 5 eV.[43] Still, the difference in O_2 and CO_2 ionization potentials is 1.7 eV, so the transfer of positive charge to O_2 is very favorable. Both of these reactions are exothermic electron-transfer reactions, and one could look to the Marcus electron transfer theory for clues as to the difference between them.

The essential result of the Marcus theory and its extensions can be expressed in terms of a rate (W) given in the form[44]

$$W = \frac{|V|^2}{h}\left(\frac{\pi}{E_r k_B T}\right)^{1/2} \sum_{n_f} S(0,n_f) \exp\left[\frac{(\Delta G + E_r + n_f w)^2}{4E_r k_B T}\right] \quad (10)$$

where ΔG is the free energy of the electron-transfer reaction, E_r is the so-called solvent reorganization energy, V is the electronic matrix element for electron transfer, and $S(0,n_f)$ is the Franck−Condon factor. The sum is taken over quantized vibrational states of the product with energies $n_f\omega$.

In terms of this rate expression, energy of the reaction of $C_2O_4^+$ with DMA is much greater than the minimum energy requirement, i.e., $-\Delta G > E_r$,[27] and at any given energy, many excited electronic and vibrational states of the product can be found to satisfy the energy matching criterion $\Delta G = -n_f\omega$, which optimizes the electron-transfer probability. In the case of O_2 reaction with $C_2O_4^+$, a similar argument might apply. However, O_2 has only a single vibrational degree of freedom and there are no allowed electronic states available. Thus, the electron-transfer for the reaction between $C_2O_4^+$ and O_2 will be less efficient and may not occur at each encounter. We note that there is still a factor of 2 variation in the rate of the oxygen reaction over the density range we investigated. The origin of this variation will be difficult to interpret until ionic mobilities are known with certainty.

Conclusion

In this paper, we have shown that short-lived radical ions, $C_2O_4^+$ and $(CO_2)_n^-$, are generated upon radiolysis of $scCO_2$. The charge-transfer reactions of $(CO_2)_n^-$ with BQ and $C_2O_4^+$ with DMA are at or near the diffusion-controlled limit for $\rho_r < 1$ and exhibit strong dependence of the rates on the bulk density of $scCO_2$. Considering the reasonable approximations we used for calculating the diffusion-controlled rates, the correlation between theoretical and experimental values for rate constants is shown to be good for $\rho_r < 1$. At higher densities, the decrease in mobility of radical ions coupled with possible changes in solvent reorganization energy alters the reaction rates. On the other hand, the rate of electron-transfer reaction between O_2 and $C_2O_4^+$ is below the diffusion-controlled limit. Changes in the bulk density of $scCO_2$ have little effect on the rate of reaction.

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