Pulse radiolysis studies in supercritical CO$_2^+$

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Introduction

One question of great interest is the nature of chemical reactivity in supercritical fluids: are there different reaction mechanisms that are important in supercritical fluids. For example in normal solutions, it is assumed that the solvent reorganization energy is more important in electron transfer reactions than the role of solvent fluctuations. However, in supercritical fluids, the much larger fluctuations may make the fluctuations an important component in fast reactions.

To study such effects, it is important to measure the kinetics of fast reactions. Various kinetic techniques are available for such studies. These include emission spectroscopy where the rates are measured by the efficiency of excited-state quenching; flash photolysis¹ and pulse radiolysis²,³.

Because of our experience with pulse radiolytic techniques, we have chosen to use that technique. In pulse radiolysis, one uses a short pulse of ionizing radiation to initiate the reactions. The ionizing radiation (normally a pulse of high energy electrons, 3-20 MeV) will interact with the electrons in the system. Because most of the electrons will be in the solvent, the solvent will be ionized. In practice one will then get ions and radicals of the solvent. These can interact with the solute. In essence, then, the technique is similar to flash photolysis, but the chemistry is initiated in the solvent rather than in the solute. A more complete description of radiation chemistry is available in the reference.⁴
In this work we measured the absorptions that were generated in supercritical CO$_2$ from 3-1000 ns. From these measurements we were able to show that the C$_2$O$_4^+$ cation was formed. We also showed that ozone could be formed after several pulses; we shall not discuss those results here. We then added small concentrations of dimethyl-aniline (DMA) and observed the kinetics of the decrease of the concentration of C$_2$O$_4^+$. We followed the reaction of the anion with benzoquinone (BQ) by observing the kinetics of the benzoquinone anion. We also measured the reaction of O$_2$ with C$_2$O$_4^+$. These experiments were run as a function of CO$_2$ pressure.

**Experimental**

All chemicals were of the highest purity commercially available. The CO$_2$ was SFC grade-diptube and was purified by passing it through a dry-ice trap to remove trace amounts of water. Solid samples such as p-benzoquinone and p-chloranil were dissolved in ether. The desired amount of the solution was added to the open cell and the ether was evaporated. The cell was then evacuated and pressurized. For liquid samples such as N,N-dimethylaniline, the cell was purged using CO$_2$. The liquid sample was then added to the cell and the cell was immediately closed and pressurized. Gases were added by evacuating the cell, putting the desired amount of the reactant gas in the system and then pressurizing the cell.

Experiments were performed in a stainless-steel cell with Suprasil windows. The windows were 1 cm thick and were sealed to the cell using Teflon o-rings. The optical length of the cell was 5 cm. All experiments were run at 40.1 ± 0.1°C ($T_r = 1.03$). The pressure in the cell was adjusted using an HPLC pump (JASCO, Model PU-980). The details of the experiment are similar to those that have been previously described.$^5,^6$

The pulse radiolysis experiments were done using the Argonne 20 MeV linear electron accelerator with pulse widths from 30 ps to 40 ns. The energy of the pulse was between 18-20 MeV. Irradiations were carried out with colinear beam and optical paths. A conventional “rule-of-thumb” is that electrons lose energy at a rate of approximately 2 MeV per centimeter/(density of material in g/cm$^3$). Therefore only about 5 MeV would be lost in the input window and there is no difficulty irradiating the sample. Using Plexiglas (poly-methyl-methacrylate) as a dosimeter, the distribution of the dose was determined in the cell.$^7$ There is about a factor of 20 difference between the dose at the beginning of the cell and at the end of the cell. The dose distribution is only weakly dependent on the density of the fluid in the cell. Details of these measurements have been published previously.$^5$ Because all measurements used pseudo-first-order kinetics, the dose distribution does not affect the measured kinetics. The dose in the cell was approximately 7.6 $\rho$Gy for the 30 ps pulse and 27.5 $\rho$Gy for the 4 ns pulse, where $\rho$ is the density in g/cm$^3$ and Gy is gray or 1J/kg energy deposited (100 rads = 1 Gy).
A pulsed xenon arc lamp (75 w, pulsed for approximately 500 μsec) was used as an optical probe. The light was isolated using either a monochromator (250-450 nm) or interference filters (10 nm or 40 nm width) from 400-1000 nm. The light was detected using a R-928 Hamamatsu photomultiplier (used in a 5-dynode configuration) or a silicon photodiode (EG&G FND-100). The data were acquired using a Tektronix TVS 645A digitizer (1Ghz bandwidth, 5 Gsamples/sec digitizing rate).

The kinetic data were analyzed using a non-linear least-square fitting routine for the optical absorption data. The PVT relationships for sc-CO₂ were evaluated using the BWR equation.⁸

Results and discussion

The radiolysis of gaseous CO₂ has been studied⁹-¹² and mechanisms have been proposed for the radiolysis products¹³. The initial ionization will produce the cation radical CO₂⁺ (and possibly CO⁺, C⁺, and O⁺, albeit with lower yields) and e⁻. The electron will be ejected with a range of energies, and with the most probable energy range of 20-100 eV. These electrons can create more ionization. The thermalization distance for the electron will depend on the density of the fluid as will the distance between ionization locations. For a density of 0.5 g/cm³, the separation will be approximately 1000 nm between primary ionization events.

Figure 1 shows the absorption spectrum that is observed in pure supercritical CO₂. Also shown in the figure is the photoionization spectrum that has been assigned to C₂O₄⁺.¹⁴ There appears to be a good correlation between the spectra in the blue region of the spectrum, suggesting that the C₂O₄⁺ species is formed very quickly. To confirm this assignment, we looked at the yield of the 700 nm band as a function of added SF₆, a known electron scavenger. In the presence of the SF₆, the absorption increased, further confirming the assignment of the absorption to a positive ion. Further evidence that the species is charged comes from the density dependence of the absorption. The amount of absorption increased as the density decreased. This
is not what one might intuitively expect because the amount of ionization will be proportional to density. As we have shown previously, this behavior is what one would expect for an ion if there is geminate recombination from the cation and the electron. To summarize that discussion: as the density decreases, the thermalization distance of the electron will increase. This means that the electron will go farther from the cation. At the Onsager distance, the coulombic attraction will be equal to the thermal energy, which means that the recombination will decrease.

Reactions of anions One of our first goals was to measure the reaction of the anionic species as a function of reaction energy. We hoped that it would be possible to learn about the role of solvent fluctuations from these tests. It is known that the electron will react very quickly with CO2 in liquids but only slowly in gases. The low reaction rate in gases arises because the CO2 ground state is linear while the CO2- is bent. It has been shown that the energetically most-favored dimer anion is a bent CO2- anion that is solvated by a linear CO2. It has been shown that the anion-product is stable in both polar and non-polar media and that the product can transfer an electron to an appropriate reactant.

We have attempted to measure the absorption spectrum of the anion species in CO2; however we were unable to observe the spectrum of the anion. We thus measured the kinetics by the production of the anion. The lifetime of the anions is limited in the SC-CO2 system, presumably by ion-recombination reactions. Thus to make meaningful measurements, it is necessary for the electron transfer reaction to be sub-100 nanoseconds. This means that the concentration of the reactant must be nearly 1 mM. The relatively high electron affinity ($E^0 = -0.54$ V vs. SCE) makes the reaction

$$(CO_2)_2 + BQ \rightarrow BQ^- + nCO_2$$

strongly exothermic. Figure 2 shows the product spectrum at 60 nsec after the pulse. The spectrum of the BQ- is clearly seen. An inset to the figure shows the kinetics as a function of CO2 pressure. Typical kinetic data are shown in figure 3. Figure 3a shows the kinetics as a function of benzoquinone concentration. The pseudo-first-order rate constants were determined by fitting the growth and decay of the BQ-.
order rate constants as a function of benzoquinone concentration. The curves were linear over the entire pressure studied. Figure 3b shows the density dependence of the yield of BQ\textsuperscript{−} and the yield of the BQ\textsuperscript{−}. Because we are measuring pseudo-first-order rates, we are not concerned about the concentration dependence. The pressure dependence of the yield of BQ\textsuperscript{−} is to be expected. As discussed previously, the ion-recombination mechanism will lead to a loss of both the cation and anion.

While we know that the electron transfer reaction (1) has occurred, it is unclear what the value of "n" is. In gas-phase cluster experiments, negative clusters have been formed, but the size of the cluster depends on the electron energy. It is difficult to know how to translate these results into the fluid phase.\textsuperscript{22,23,17,24}

We had intended to study these reactions as a function of redox potential of the reactant. Unfortunately, most of the well-known electron transfer candidates were insoluble in the sc-C\textsubscript{O}\textsubscript{2}. We attempted to study the reaction of the chloranil; however, we were unable to isolate the spectrum of the anion. It appeared as if the excited state was formed.

Reactions of cations: Above we discussed the formation of the cation C\textsubscript{2}O\textsubscript{4}\textsuperscript{2+}. We measured the reactivity of this species with N,N-dimethyl aniline (DMA) and oxygen. The kinetics were measured by observing the decay of the C\textsubscript{2}O\textsubscript{4}\textsuperscript{2+} species at 700 nm. The pseudo-first-order plots were linear over the concentration range studied.

Discussion of kinetics The rate constants that have been determined for BQ and DMA are in the range of 10\textsuperscript{11}/mole-sec, rates that are characteristic of activationless or diffusion-controlled reactions. Diffusion-controlled reactions can be considered in two limits; at low densities, the rates depend only on the encounter radii and not on the diffusion constant. At higher densities, the rates can be described by the Smoluchowski equation

\[ k_{\text{diff}} = 4\pi LDR \]
where \( \text{L} \) is Loschmidt's constant, \( \text{R} \) is the reaction radius and \( \text{D} \) is the diffusion constant. The application of this formula to supercritical solutions is limited by the determination of diffusion constants. Fortunately, for sc-CO\(_2\) there are considerable data on diffusion constants and theoretical and semiempirical relationships exist\(^{25,26}\). We have made use of these relationships to estimate the diffusion constants for \( \text{C}_2\text{O}_4^+ \), \( \text{C}_2\text{O}_4^- \), DMA and benzoquinone as functions of pressure. No data exist for the ionic species and experimental data suggest that the diffusion constants for the ions are different from the neutral species. In addition the ratio of the diffusion constant of the neutral to the charged species appears to vary as a function of pressure\(^{27}\).

Figure 4 shows the rate constants for \( \text{C}_2\text{O}_4^+ + \text{DMA} \); \( \text{C}_2\text{O}_4^+ + \text{O}_2 \); and \( \text{C}_2\text{O}_4^- + \text{BQ} \) as a function of density. Also shown on the figure are the estimated diffusion-controlled rates. The assumed reaction radius was 6.5\( \text{Å} \). We expect that the calculated rate constants will be upper limits, because, as discussed above, the diffusion constant that we used is almost certainly an upper limit. There are two reasons for the difference between the calculated and measured rate constants at high densities for the reactions of \( \text{C}_2\text{O}_4^+ + \text{DMA} \) and \( \text{C}_2\text{O}_4^- + \text{BQ} \). The diffusion constants decrease more quickly at high densities for the ions than we predict or that the energy for the reaction is lower. There is experimental evidence that the diffusion constant for an anion molecule decreases more quickly than the diffusion constant for the corresponding neutral for reduced densities \( 1 - 2 \) (which is equivalent to \( 1/\rho \), between 0.5 and 1.0)\(^{27}\). The magnitude of the difference between the expected and the measured rate constants for the cation suggests that this factor may completely explain the cation reaction. The decrease in the rate of the anion is larger. As discussed above, the anion cluster depends on many factors, including density. If the anion cluster is bigger, the electron will be better solvated and thus there will be less energy available for the reaction.

The reaction \( \text{C}_2\text{O}_4^+ + \text{O}_2 \) is approximately a factor of ten below the diffusion-controlled limit. While there is less energy available for this reaction, there is still a considerable excess. One possible explanation is that we are in the "Marcus Inverted Region", which would then lower the rates. For the DMA or BQ, there are a considerable number of excited ionic and vibrational states that can dissipate the excess energy; while for \( \text{O}_2 \) the only a limited number of states available.
Summary and Conclusion

In this paper we have shown the ability of pulse radiolysis to study the rates of electron-transfer reactions in supercritical solutions. We have shown that for aromatic reactants with considerable energy available, the reactions are at or near the diffusion-controlled limit. At higher densities, the rates may be below the diffusion-controlled limit, although this conclusion is limited by the availability of reliable diffusion constants. We hope to explore these measurements further with the use of appropriate reactants that can be dissolved at sufficiently high concentrations in sc-CO$_2$.

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