Enhanced Cage Effects in Supercritical Fluid Solvents. The Behavior of Diffusive and Geminate Caged-Pairs in Supercritical Carbon Dioxide

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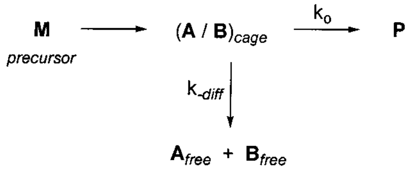
Abstract: The behavior of geminate and diffusive radical caged-pairs arising from the photolysis of dicumyl ketone in conventional and supercritical carbon dioxide (SC−CO_2) solvents has been examined. The results suggest that locally enhanced solvent density about a solute (solvent/solute clustering) can lead to an enhanced cage effect near the critical pressure in supercritical fluid solvents. This enhanced cage effect is similar in magnitude for both diffusive and geminate caged-pairs.

There is a need to reduce or eliminate toxic chemical waste and/or byproducts which arise in the course of chemical synthesis and manufacture.[1] One way to accomplish this is to replace toxic, environmentally threatening solvents utilized in many chemical processes with nontoxic, "environmentally-benign" alternatives. Supercritical carbon dioxide (SC−CO_2) has emerged as a suitable, "environmentally benign" alternative for a variety of solvents.[2,3] The supercritical state of CO_2 is easily attained ($T_c = 31$ °C, $P_c = 74$ bar),[4] and being nontoxic, CO_2 is a viable alternative to traditional solvents which are either carcinogenic (e.g., benzene) or damaging to the environment (e.g., CFC's, CCl_4).

For these reasons, there is considerable interest in the physical aspects of chemistry conducted in supercritical fluid (SCF) solvents. In addition to the considerations discussed above, there are several advantages associated with the use of supercritical fluids as solvents for chemical reactions from the standpoint of reactivity and selectivity. Changes in rate arising from the direct effect of pressure (and temperature) are governed by transition state theory, and pertain to reactions in both SCF medium and conventional solvents. However, what is special about SCF solvents is that important solvent parameters such as dielectric constant, viscosity, and solubility parameter vary dramatically with temperature and pressure,[5,6] thereby providing a unique element of control over the kinetics of a chemical process.[7]

Scheme 1



Solvent viscosity is one example of a manipulable parameter that can affect the outcome of a chemical process. For example, consider two highly reactive species **A** and **B** generated simultaneously in a solvent cage as a *geminate* caged-pair from a common precursor molecule **M** (Scheme 1). Further, suppose that reaction within the (**A**/**B**) caged-pair gives rise to a unique product **P** and the rate constant for this process is k_o; counter-diffusion ($k_{-\mathrm{diff}}$) yields *free* **A** and **B**, which give rise to different products. Because the magnitude of $k_{-\mathrm{diff}}$ is related to solvent viscosity, increased viscosity will favor production of product **P** ($k_{-\mathrm{diff}} < k_o$), while at lower viscosity, products arising from individual reactions of free **A** and free **B** will be formed. According to the Noyes model, the ratio of products arising from the k_o and $k_{-\mathrm{diff}}$ pathways varies linearly with the inverse of viscosity ($1/\eta$.)[8]

Rather than being formed from a common precursor, a *diffusive* caged-pair is produced by diffusion of *free* **A** and *free* **B** together (with diffusion-controlled rate constant k_{diff}), i.e., $\mathbf{A}_{\mathrm{free}} + \mathbf{B}_{\mathrm{free}} \rightarrow (\mathbf{A}/\mathbf{B})_{\mathrm{cage}}$. Thus, while a geminate caged-pair may have a history associated with it (i.e., the orientation of **A** and **B** with respect to each other and the solvation shell may be similar to the precursor), the orientation within a diffusive caged-pair will be random. In accordance with theory, the diffusion-controlled rate constant k_{diff} is expected to vary linearly with inverse viscosity.[9]

The viscosity of a supercritical fluid varies dramatically with pressure and temperature. For CO_2 at 37 °C, a change in pressure

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from just above the critical pressure (74 bar) to 300 bar results in a change in viscosity from 0.02 to 0.12 cP.[10] Thus, for reactions which are sensitive to solvent viscosity, a relatively small variation in pressure may significantly influence the outcome of the reaction. However, because of the unique nature of supercritical fluids, there are yet *additional* factors which may lead to deviations in rate/viscosity correlations, specifically the possibility that cage lifetimes may be enhanced at pressures near the critical point.

It has been suggested that cage lifetimes may be enhanced near the critical point because of an increase in the local solvent density around the solute.[11,12] This phenomenon, known as "solvent/solute clustering", is well-documented, particularly in the spectroscopic literature.[13−23] In addition, there is good evidence to suggest that such clustering may affect the rates of chemical phenomena.[17,18,24−30] It is thus reasonable to suppose that increased local solvent density (and implicitly, increased local viscosity) about $\mathbf{A}_{\mathrm{free}}$, $\mathbf{B}_{\mathrm{free}}$, or $(\mathbf{A}/\mathbf{B})_{\mathrm{cage}}$ would diminish k_{diff} and/or $k_{-\mathrm{diff}}$ to a greater extent than expected based upon bulk solvent properties.

There are a number of seemingly contradictory reports in the literature pertaining to enhanced cage lifetimes near the critical point in SCF solvents.[31−38] For example, Andrew et al. examined the photo-Fries rearrangement of naphthyl acetate in SC−$\mathrm{CO_2}$.[35] Near the critical pressure, an enhanced cage effect was observed that was attributed to solvent/solute clustering. In contrast, for the free radical chlorination of alkanes, there was no indication of an enhanced "chlorine atom cage effect" near the critical pressure in SC−$\mathrm{CO_2}$ solvent.[37,38] Moreover, the magnitude of the cage effect observed in SC−$\mathrm{CO_2}$ at all pressures examined was within what is anticipated based upon extrapolations from conventional solvents.

Assuming that enhanced cage effects near the critical point in supercritical fluids are the consequence of clustering and not experimental artifacts, then the important issue to address is why are they observed in some cases, but not in others. There are two likely explanations: The magnitude of the effect may be related to the strength of the interaction between the solute(s) and solvent (i.e., specific functional groups on **A** or **B** may interact more strongly with solvent). In the case of geminate caged-pairs, interactions between the *precursor molecule* **M** and the solvent may lead to formation of a cluster into which the **A**/**B** pair is born.

It is possible that enhanced cage effects arising from solvent/solute cluster formation may be especially important in systems which possess aromatic rings. The local solvation behavior of aromatic compounds (specifically naphthalene,[39] benzene, and toluene)[40] in SC−$\mathrm{CO_2}$ has been examined theoretically, and has been found to form ordered structures with $\mathrm{CO_2}$. Hence it is possible that because of the naphthalene ring, solvent/solute clustering led to the enhanced cage effect observed in the photolysis of naphthyl acetate. For the chlorine atom cage effect study, because there was no specific functional group for $\mathrm{CO_2}$ to interact strongly with, there was little or no local density enhancement near the critical pressure. Consequently, an enhanced cage effect was not observed.

To test these hypotheses, cage effects were examined in a system (a) that possesses aromatic rings and (b) that generates *both* a diffusive and geminate caged-pair (each of which give rise to unique products). In this chemistry, a geminate caged-pair is formed by photolysis of a ketone: $\mathrm{RCOR} \rightarrow (\mathrm{R}\bullet/\bullet\mathrm{COR})$. A diffusive caged-pair is formed by the self-reaction of R•: $2\mathrm{R}\bullet \rightarrow (\mathrm{R}\bullet\ \bullet\mathrm{R})$.

Alkyl radical pairs react either via dimerization (k_{dim}) or disproportionation (k_{disp}) pathways: $2\mathrm{R}\bullet \rightarrow \mathrm{R{-}R}$ and/or $\mathrm{R_{-H}} + \mathrm{R_{-H}}$. Fischer demonstrated that for *diffusive tert*-butyl radical caged-pairs in a series of *n*-alkane solvents, the rate constant ratio ($k_{\mathrm{dim}}/k_{\mathrm{disp}}$) varies as a function of solvent viscosity.[41,42] Thus, the rate constant ratio $k_{\mathrm{dim}}/k_{\mathrm{disp}}$ is a sensitive probe for cage effects involving a diffusive caged-pair. Cumyl radicals self-react at a diffusion-controlled rate constant ($2k_{\mathrm{T}} = 1.6 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$),[43] yielding cumene and α-methylstyrene (disproportionation) and bicumyl (dimerization), with $k_{\mathrm{disp}}/k_{\mathrm{dim}} = 0.05$.[8] Accordingly, this paper describes the behavior of geminate and diffusive radical pairs, generated via photolysis of dicumyl ketone, in supercritical solvent as a probe for enhanced cage effects near the critical point.

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Scheme 2

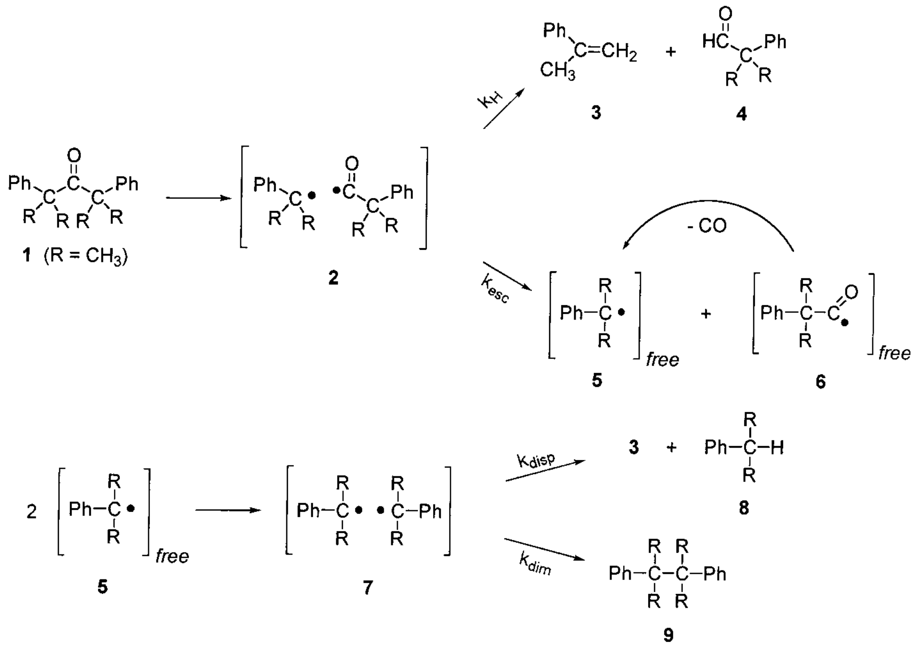

Table 1. Photolysis of Dicumyl Ketone in Conventional Solvents at 50 °C

solvent	η (cP)	**9** (μmol)	**8** (μmol)	**4** (μmol)	k_{dim}/k_{disp}	k_{esc}/k_H
hexane	0.24	9.96	0.375	0.177	26.6	58.4
heptane	0.30	11.2	0.5	0.291	22.4	40.2
octane	0.38	8.30	0.509	0.236	16.3	37.3
CCl_4	0.71	2.88	0.193	0.154	14.9	20.0
$C_2F_2Cl_4$	0.91	3.33	0.212	0.129	15.7	27.5

Table 2. Photolysis of Dicumyl Ketone in Supercritical Carbon Dioxide at 50 °C

pressure (psi)	η (cP)	**9** (μmol)	**8** (μmol)	**4** (μmol)	k_{dim}/k_{disp}	k_{esc}/k_H
1110	0.0205	5.32	0.282	0.237	18.9	23.6
1125	0.0207	4.39	0.240	0.211	18.3	21.9
1130	0.0208	5.63	0.314	0.174	17.9	34.2
1134	0.0208	4.02	0.230	0.174	17.5	24.4
1230	0.0225	8.25	0.378	0.324	21.8	26.6
1305	0.0241	7.01	0.286	0.271	24.5	26.9
1390	0.0263	6.04	0.235	0.136	25.7	46.2
1465	0.0305	4.96	0.163	0.071	30.5	72.2
1473	0.0310	3.00	0.082	0.029	36.6	106
1560	0.0358	3.64	0.106	0.030	34.4	125
1600	0.0378	9.18	0.295	0.120	31.1	79.0
1728	0.0433	6.04	0.192	0.066	31.5	94.4
1756	0.0444	7.95	0.255	0.070	31.2	117
2134	0.0557	6.03	0.188	0.059	32.1	106
2644	0.0656	6.41	0.208	0.069	30.8	95.8
2740	0.0670	5.53	0.174	0.063	31.8	90.5
3946	0.0814	6.29	0.227	0.086	27.7	75.8
4005	0.0820	4.33	0.159	0.061	27.2	73.5
6194	0.101	9.89	0.418	0.165	23.7	62.5
7456	0.110	6.34	0.297	0.121	21.4	54.9
7936	0.114	4.77	0.247	0.124	19.3	40.5
8534	0.118	5.27	0.307	0.144	17.1	38.7

Results and Discussion

Solubility of Dicumyl Ketone in SC−CO$_2$. Because SC−CO$_2$ is nonpolar, polar compounds tend not to be very soluble (especially at lower pressures where the dielectric constant and Hildebrand solubility parameter are low). To ensure that the results of these experiments would not contaminated by unanticipated and unnoticed phase behavior, it was deemed critical to examine the solubility behavior of dicumyl ketone in SC−CO$_2$ at the same concentration that would be used in this study, and especially, at pressures nearing the critical pressure.

Solubility was checked using a view cell. The starting ketone was dissolved in a tiny quantity of diethyl ether, and the resulting solution was placed on one of the sapphire windows of the view cell to create a film. The view cell was assembled, the system was pressurized with CO$_2$ and equilibrated at the desired temperature and pressure, and the dissolution of the starting material was observed visually. Without agitation, it was found that the starting material was fully dissolved in less than 25 min.

Reaction Mechanism. Photolysis of dicumyl ketone (0.01 M in either conventional solvents or SC−CO$_2$) yields the products depicted in Scheme 2 (compounds **3**, **4**, **8**, and **9**). The results are summarized in Tables 1 and 2. Reactions were run to low (<8%) conversion to avoid further reaction of the primary reaction products. In addition to the expected products arising from dimerization and disproportionation of the cumyl radical (i.e., **9** from dimerization; **3** and **8** from disproportionation), significant yields of aldehyde **4** were produced.

Aldehyde **4** is formed as the result of hydrogen abstraction by an intermediate acyl radical produced by the Norrish I photocleavage of **1**. This acyl radical is very short-lived (the rate constant for decarbonylation is 2 × 10^8 s^{-1})[44,45] and it is unlikely that the aldehyde is formed by reaction of *free* acyl radical **6** because (a) there is not a good hydrogen atom donor present and (b) reactions are run to low percent conversion (meaning that the reaction products are not formed in sufficiently high yields to serve as H-atom donors). The fact that the yield of aldehyde varies as a function of viscosity (vide infra) strongly supports the suspicion that aldehyde **4** is formed via a cage process.

A somewhat simplified mechanism for decomposition of **1** is summarized in Scheme 2. Norrish Type I photocleavage yields a geminate acyl radical/cumyl radical caged-pair (**2**), which can either diffuse apart (k_{esc}, inevitably leading to two *free* cumyl

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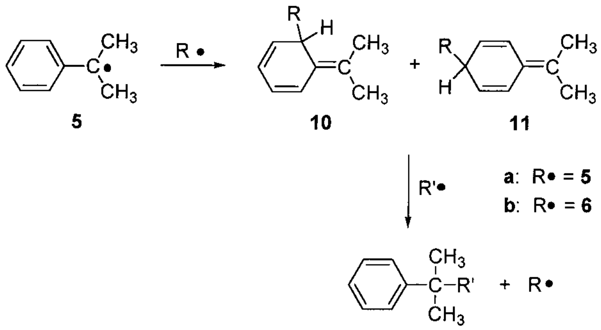
Scheme 3



radicals) or undergo in-cage reaction (k_H) yielding α-methylstyrene (**3**) and aldehyde **4**. Bimolecular reaction of free cumyl radicals leads to diffusive caged-pair **7**, giving rise to disproportionation and dimerization products, **3** + **8** and **9**, respectively. Thus, this system is especially interesting in that it allows the behavior of *two* caged radical pairs to be monitored: the *geminate* acyl radical/cumyl radical pair (**2**) and a *diffusive* cumyl radical pair (**7**).

The mechanism for the photolysis of **1** is actually a bit more complicated than that depicted in Scheme 2. In addition to the benzylic (α) carbon, radicals can couple with cumyl radical at the ortho and para positions yielding semibenzenes. The semibenzenes are known to decompose via a free radical, addition/elimination pathway (Scheme 3).[46]

Thus, in addition to dimer **9**, cumyl radical caged-pair **7** also leads to small amounts of α-ortho and α-para coupling products, **10a** and **11a**, respectively. In our runs, these compounds were detected by GC/MS, formed in quantities comparable to earlier reports,[46] and not included in the calculation of k_{dim}/k_{disp}.

Similarly, for geminate acyl radical/cumyl radical caged-pair **2**, CIDNP studies suggest that caged-pair **2** also combines regenerating **1** and also forming α-*p*-semibenzene **11b**.[47] It is thus conceivable that small amounts of dimer **9** may actually result from geminate acyl radical/cumyl radical caged-pair **2** via cumyl radical addition to **11b**. However, it is expected that this problem is minor because (a) these reactions were carried out in dilute solution and to low percent conversion and (b) the *gem*-dimethyl groups on **11b** should retard the rate of addition (steric effects).

Behavior of the Geminate Acyl Radical/Cumyl Radical Caged-Pair 2. For **2**, the rate constant ratio k_{esc}/k_H is proportional to the yield of products formed in-cage relative to those formed via reaction of free cumyl radicals (k_{esc}/k_H = ([**8**] + [**9**])/[**4**]). Because α-methylstyrene (**3**) is formed *both* by reaction of geminate caged-pair **2** and by the disproportionation of cumyl radicals, this product is uninformative in the determination of k_{esc}/k_H (or k_{disp}/k_{dim}). The trend in k_{esc}/k_H observed in conventional solvents (Table 1) supports the supposition that aldehyde **4** is formed via a cage process...higher viscosity favors aldehyde formation (in-cage); lower viscosity favors products arising from the free cumyl radical.

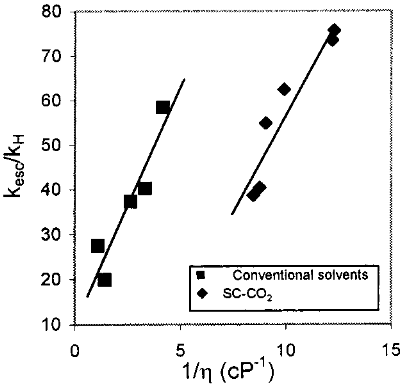


Figure 1. Partitioning of geminate caged-pair **2**: k_{esc}/k_H vs $1/\eta$ in conventional solvents and SC−CO$_2$.

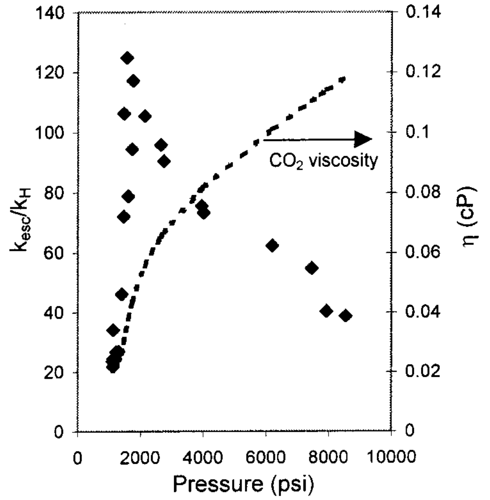


Figure 2. Partitioning of geminate caged-pair **2** in SC−CO$_2$: k_{esc}/k_H vs pressure.

The behavior of geminate caged-pairs is typically quantified in terms of the Noyes model. Koenig and Fischer[8] derived a general expression based upon the Noyes model (eq 1), where F = (1/cage efficiency) − 1, R_o is the separation between the two reactive components of the caged-pair, α the probability (per collision) that the components will react, and η the viscosity of the solvent. A_E and A_T are constants which incorporate terms pertaining to the mass, radius, and translational energy of the components of the caged-pair, and b is the diffusional radius.[8]

$$F = \frac{R_o - 2b}{2b} + \frac{R_o}{2b}\left[\frac{A_T + \alpha A_E}{\alpha}\left(\frac{1}{\eta}\right) + \frac{A_T A_E}{\alpha}\left(\frac{1}{\eta}\right)^2\right] \tag{1}$$

Equation 1 predicts that F will vary linearly with $1/\eta$, except perhaps at low viscosities where upward curvature may be observed if the $1/\eta^2$ becomes important. Cage efficiency represents the fraction of reaction that occurs within the cage, and applied to Scheme 2 is equal to $k_H/(k_H + k_{esc})$; $F = k_{esc}/k_H$. As anticipated based upon the Noyes model, in conventional solvents k_{esc}/k_H varies linearly with inverse viscosity ($1/\eta$, Figure 1).

In SC−CO$_2$ solvent, the value of k_{esc}/k_H was examined as a function of pressure at constant temperature (50 °C), and the rate constant ratio k_{esc}/k_H was found to be pressure dependent. At high pressures (>1800 psi), k_{esc}/k_H decreases smoothly with increasing pressure (Figure 2). This observation makes sense because the viscosity increases with increasing pressure (dashed line in Figure 2), and thus, the rate constant for diffusion of the species out of the cage (k_{esc}) decreases. However, a significant divergence is noted at lower pressures. At pressures less than ca. 1800 psi, the rate constant ratio k_{esc}/k_H begins to *decrease* with decreasing pressure (reaching values similar to that observed at higher bulk viscosities).

Ignoring the deviation observed near the critical point for the moment, the magnitude of the cage effect in SC−CO$_2$ is greater than expected based upon extrapolations from conven-

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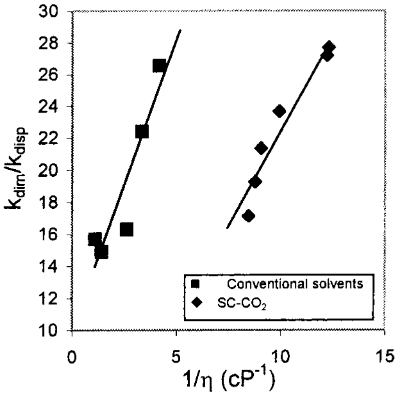
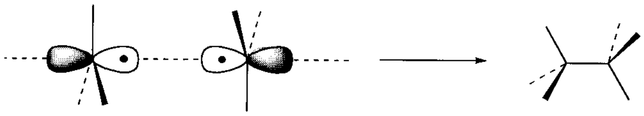


Figure 3. Partitioning of diffusive caged-pair **7**: k_{dim}/k_{disp} vs $1/\eta$ in conventional solvents and SC−CO$_2$.

Scheme 4



tional solvents. This point is illustrated in Figure 1 which plots k_{esc}/k_H vs $1/\eta$ for both conventional and SC−CO$_2$ solvents (excluding data points near the critical pressure in SC−CO$_2$). In SC−CO$_2$, although k_{esc}/k_H varies linearly with $1/\eta$ as expected, the magnitude of the rate constant ratio is about half that expected based upon the results in conventional solvents.

Behavior of the Diffusive Cumyl Radical Caged-Pair 7. For **7**, the rate constant ratio k_{dim}/k_{disp} is directly related to the yields of disproportionation vs dimerization products (k_{dim}/k_{disp} = [**9**]/[**8**]). In conventional solvents, k_{dim}/k_{disp} is found to decrease with increasing viscosity (Table 1), and k_{dim}/k_{disp} varies linearly with inverse viscosity (Figure 3). These observations are consistent with the behavior of diffusive *tert*-butyl radical caged-pairs in conventional solvents as reported by Fischer, who also found dimerization decreased with increasing viscosity.[42]

The reason that k_{dim}/k_{disp} varies with viscosity is because for dimerization to occur, the combining radicals must line up along the principal axis and reorientation (rotation) of the radicals in the caged-pair may be required (Scheme 4). As viscosity increases, this rotation is hampered (k_{dim} decreases with increasing viscosity). In contrast, the geometric requirements for disproportionation are less stringent; k_{disp} is less sensitive to viscosity.[42]

In SC−CO$_2$, diffusive cage-pair **7** behaves as expected at pressures >1800 psi: k_{dim}/k_{disp} decreases with increasing pressure (increasing viscosity, Figure 4). Excluding data at pressures <1800 psi, a plot of k_{dim}/k_{disp} vs $1/\eta$ (Figure 3) is linear, but the magnitude of k_{dim}/k_{disp} in SC−CO$_2$ is about half that expected based upon extrapolations from conventional solvents. At lower pressures (<1800 psi), anomalous behavior is observed: k_{dim}/k_{disp} decreases with decreasing pressure; near the critical pressure, the observed k_{dim}/k_{disp} values are similar to those observed at higher viscosities (Figure 4).

Cage Effects in SC−CO$_2$ vs Conventional Solvents. Photolysis of dicumyl ketone in both conventional and SC−CO$_2$ solvents yields unique products which arise from two discrete radical−radical caged-pairs. Geminate caged-pair **2** partitions between two pathways, cage-escape and hydrogen abstraction (k_{esc}/k_H); diffusive cumyl radical caged-pair **7** undergoes dimerization and disproportionation (k_{dim}/k_{disp}). In SC−CO$_2$, as measured by the variation in both k_{esc}/k_H and k_{dim}/k_{disp} with pressure, (a) the rate constant ratios vary linearly with inverse viscosity (as anticipated), but are about 2−3 times less than predicted on the basis of behavior in conventional solvents, and (b) divergent behavior is observed near the critical pressure (i.e., the rate constant ratios approach values observed similar to those observed at higher bulk viscosities).

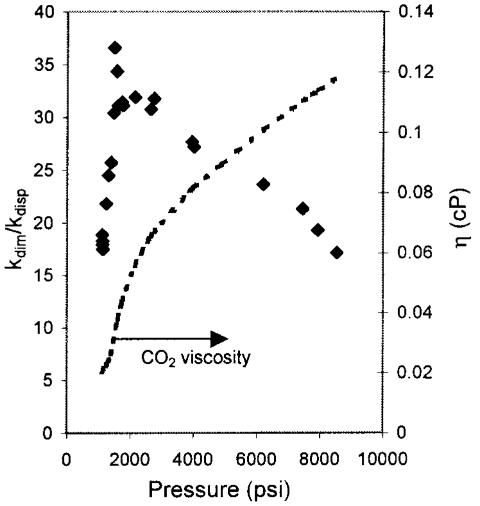


Figure 4. Partitioning of diffusive caged-pair **7** in SC−CO$_2$: k_{dim}/k_{disp} vs pressure.

An understanding of why the observed cage effects are generally larger in SC−CO$_2$ than anticipated can be achieved by considering the relationship between the diffusion coefficient of a solute, and viscosity. According to the Stokes−Einstein equation, the diffusion coefficient (D) and viscosity (η) are inversely related (eq 2, where k is the Boltzmann constant, T is the temperature in Kelvin, and r is the radius of the solute).[9] On the basis of eq 2, a plot of D vs $1/\eta$ is expected to be linear.

$$D = \frac{kT}{6\pi r\eta} \tag{2}$$

However, for SC−CO$_2$, the Stokes−Einstein equation, as well as other empirical relationships predicting an inverse relationship between D and η, tends to overestimate the diffusion coefficient of aromatic compounds (by a factor of 1.2−1.5 for benzene and 1.3−2.2 for naphthalene).[48,49] Of course the diffusion coefficient in the Stokes−Einstein equation is in reference to translational diffusion, whereas the cage effects discussed herein are related to rotational diffusion (in the case of diffusive caged-pair **7**) or separation (in the case of geminate caged-pair **2**). It is reasonable to suppose that similar (but not necessarily identical) considerations pertain.

Both k_{esc}/k_H and k_{dim}/k_{disp} deviate as the critical pressure is approached. These observations suggest that movement (translational and rotational) of the caged-pairs is impeded, and solvent/solute clustering emerges as a plausible explanation for these phenomena. (Heitz and Bright recently probed the extent of local density enhancement in the critical region in SC−CO$_2$, SC−CHF$_3$, and SC−CH$_3$CH$_3$ by examining the rotational reorientation kinetics of *N*,*N*′-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenecarboxodiimide (BTBP). Near the critical density, rotational times were longer than predicted on the basis of bulk solvent properties because of solvent/solute clustering.[29] Analogous results have been reported for other systems.)[27,28] Thus, it is reasonable to conclude that solvent/solute clustering has a

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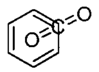
[48] Debenedetti, P. G.; Reid, R. C. *AIChE J.* **1986**, *32*, 2034−2046.

[49] Clifford, A. A.; Coleby, S. E. *Proc. R. Soc. London A* **1991**, *433*, 63−79.

similar effect on the behavior of diffusive caged-pair **7** (and $k_{\mathrm{dim}}/k_{\mathrm{disp}}$) near the critical pressure.

Although these results are consistent with the notion that the local viscosity is higher than in the bulk, it does not necessarily hold that the rate constant ratios are a *measure* of local viscosity, or that the term "local viscosity" has any meaning in this context. The structure of these clusters (if they even *have* a defined structure) is unknown, and it is possible that translational and rotational motion is not random (e.g., does motion occur within a cluster, or does the cluster behave as a single entity?). Thus, although the Noyes model provides a useful quantitative treatment of cage effects in terms of a macroscopic solvent property (i.e., viscosity), it would be unwise to overextend this theory to describe the microscopic behavior of clusters.

Nature of the Interaction between CO_2 and the Cumyl Radical. The nature of the intermolecular interaction between CO_2 and aromatic molecules was examined theoretically in order to better understand the nature of solvent/solute clusters in SC−CO_2 solvent. Using density functional theory (DFT), it was found that for the interaction of benzene with CO_2, the binding energies were 0.40, 1.12, 1.35, and 2.87 kcal/mol for the addition of one, two, three, and four CO_2's, respectively.[40] For PhH + CO_2, the structure of the complex is one in which the CO_2 molecule lies approximately 3.6 Å above the plane of aromatic ring, with one of the C−O bonds nearly lined up with a C−H bond of benzene (e.g., **12**). As more CO_2's are added, the new molecules build upon this general structure, maximizing the most favorable interactions.[40]



12

Utilizing density functional theory implemented through PC Spartan Pro (Becke-Perdew BP86 functional and DN** full polarization basis sets),[50] the interaction between CO_2 and a cumyl radical was examined. Because of the lower symmetry of the cumyl radical compared to benzene, a larger set of structures was considered. Of these, only two low-energy structures were found, both of which place the CO_2 about 3.6−3.7 Å above the aromatic ring in a manner similar to the PhH/CO_2 complex, and with binding energies of 0.24 and 0.87 kcal/mol (Figure 5a). For both of these structures, in the CO_2 portion, there is a shift of electon density toward the outer oxygen, but no net transfer of electron density from the aromatic ring to the CO_2 (i.e., these are not donor/acceptor complexes). In addition, there is no transfer of spin density from the cumyl radical to CO_2. As the spin density isosurface for this system reveals (Figure 5b), the CO_2 molecule prefers to associate with the carbons at which the spin density is the smallest.

Summary and Conclusions

This study lends support to the notion that locally enhanced solvent density about a solute (solvent/solute clustering) can result in an enhanced cage effect in supercritical fluid solvents. The degree of this enhancement depends on the magnitude of the interaction between the solvent and specific functional groups on the solute, in this case, SC−CO_2 and the aromatic ring of the cumyl radical. DFT calculations suggest that the nature of the interaction between CO_2 and cumyl radical involves polarization of one of the C═O bonds of CO_2 by the aromatic ring, but that there is no significant amount of spin and/or charge-transfer involved. The fact that an enhanced cage effect is observed both for diffusive caged-pair **7** and geminate caged-pair **2** and is similar in magnitude suggests that this phenomenon is not restricted to geminate caged-pairs which are "born" into a cluster arising from interactions between the precursor molecule (dicumyl ketone in this instance) and CO_2 solvent.

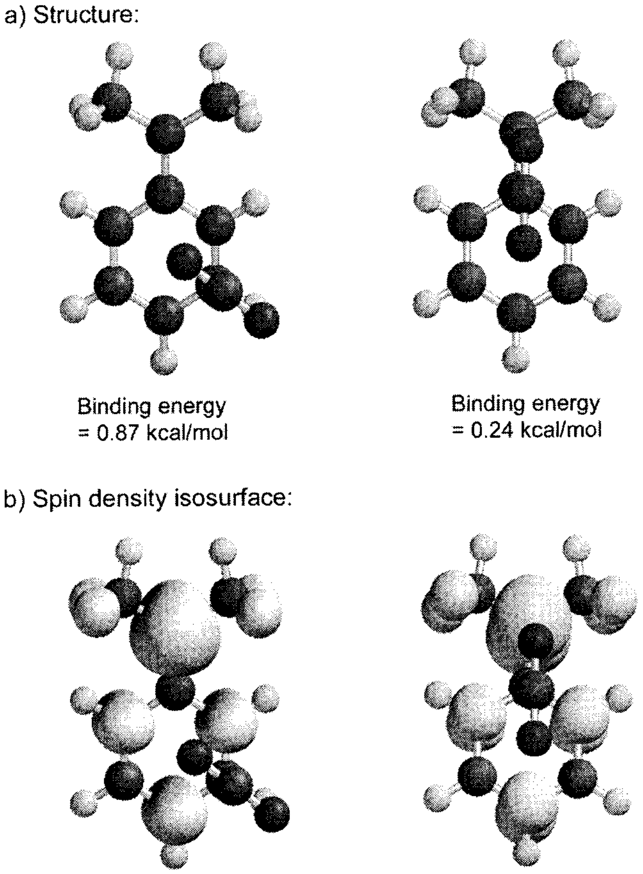


Figure 5. Structure of cumyl radical/CO_2 complexes.

Experimental Section

General Considerations. Gas chromatographic analyses were performed on a Hewlett-Packard 5890A instrument equipped with FID detection and HP 3393A reporting integrator. Analyses were conducted using either an Alltech SE-30 or SE-54 capillary column (30 m × 0.25 mm ID × 0.25 μm). Products were identified by comparison of retention time with that of an authentic sample and by GC/MS. Product yields were quantitated vs a measured internal standard and appropriate GLC correction factors. All gas chromatographic analyses were performed in triplicate.

Materials. Hexane, heptane, octane (Aldrich), CCl_4 (JTBaker), and $CFCl_2CFCl_2$ (PCR Inc.) were used as received. SFC-Grade carbon dioxide was obtained from Scott Specialty Gases. Dicumyl ketone was prepared according to literature procedures.[51]

Reactions in SC−CO_2 Solvent. The details regarding the apparatus for reactions conducted in supercritical carbon dioxide have been previously reported.[52] Briefly, the reactor is constructed of Hastelloy C-276, and is equipped with a sapphire window (for irradiation) and a

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(50) Hehre, W. J.; Yu, J.; Klunzinger, P. E.; Lou, L. *A Brief Guide to Molecular Mechanics and Quantum Chemical Calculations*; Wavefunction, Inc.: Irvine, 1998.

(51) Dyllick-Brenzinger, R. A.; Patel, V.; Rampersad, M. B.; Stothers, J. B.; Thomas, S. E. *Can. J. Chem.* **1990**, *68*, 1106−1114.

(52) Tanko, J. M.; Blackert, J. F.; Sadeghipour, M. In *Benign by Design. Alternate Synthetic Design for Pollution Prevention*; Anastas, P. T., Farris, C. A., Eds.; American Chemical Society: Washington, DC, 1994; Vol. 577, pp 98−113.

magnetic stir bar. In a typical experiment, 45.2 mg (169 μmol) of dicumyl ketone (ca. 0.01 M in SC−CO_2) was placed in a 1 mL ampule, degassed 5× (freeze−pump−thaw), and sealed. The ampule was introduced into the high-pressure reactor (50 °C) with magnetic stirring. The system was closed and purged with argon followed by CO_2 (30 min each). The system was pressurized with CO_2 (causing the ampule to rupture) and the reaction mixture was stirred overnight.

The reaction mixture was irradiated with a 150 W xenon arc lamp; the reaction time was adjusted such that the percent conversion was approximately 3−8%. After completion, the system was depressurized by bubbling the contents of the reactor through 12 mL of ethyl acetate at 0 °C. The reactor was opened and washed thoroughly with ethyl acetate. These fractions were combined and an internal standard (diphenylmethane) was added and analyzed by gas chromatography.

Reactions in Conventional Solvents. Dicumyl ketone (45.2 mg, 169 μmol) and the desired solvent were placed in a ca. 35 mL Pyrex pressure tube; the concentration of dicumyl ketone was 0.01 M. The reaction mixture was degassed 3−4× by the freeze−pump−thaw method and irradiated at 50 °C with a 150 W xenon arc lamp. After illumination, the pressure tube was cooled to room temperature, an internal standard was added, and the reaction mixture was analyzed by gas chromatography.

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