11958 J. Am. Chem. Soc. 1996, 118, 11958−11959

Communications to the Editor

Viscosity-Dependent Behavior of Geminate Caged-Pairs in Supercritical Fluid Solvent

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Received July 15, 1996

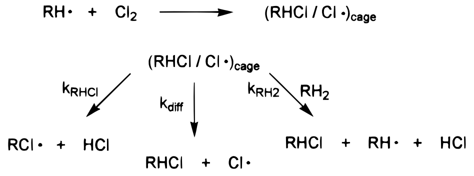
There is considerable interest in the use of supercritical fluids (SCFs) as solvents for chemical reactions. Important solvent properties of a SCF such as dielectric constant, solubility parameter, viscosity, etc. can be altered via manipulation of temperature and pressure.[1,2] Conceivably, this feature could be exploited to control the behavior (i.e., kinetics, selectivity) of a chemical reaction in a manner not feasible with conventional solvents. Supercritical carbon dioxide (SC-CO_2) is especially attractive as a reaction solvent because CO_2 is a naturally-occurring and environmentally-benign resource, and the supercritical state is easily attained ($T_c = 31$ °C; $P_c = 74$ bar) without a disproportionate expenditure of energy.

Cage effects are observed when two highly reactive species, A and B, are generated in close proximity within a solvent cavity and the rate of reaction between A and B (in-cage) is competitive with diffusion apart (cage-escape). A diffusive A/B caged-pair arises from encounter of free A and free B (i.e, a diffusion-controlled reaction), while a geminate A/B caged-pair arises when A and B are generated from a common precursor.

Because they are considerably less viscous than conventional (liquid) solvents, it might be expected that cage effects would be nominal in SCF solvent. However, one unique feature of SCF solvents is that the local density of solvent about a solute can be significantly greater than the bulk.[3] This "clustering" phenomenon becomes especially important at pressures approaching the critical pressure (P_c). Consequently, several recent studies have attempted to ascertain whether enhanced cage effects can be observed in the near-critical region for reactions involving diffusive-[4−9] and geminate-caged pairs.

With regard to the behavior of geminate-caged pairs in SCF solvent, most quantitative studies have dealt with photochemical reactions. Fox and Johnston et al. studied the photolysis of unsymmetrical dibenzyl ketones in SC-CO_2 and found no evidence for a cage effect (even in the vicinity of the critical point).[10] In a later study, these same workers found some evidence for solvent-solute clustering in the photodissociation of I_2.[11] A recent Communication on the photo-Fries rearrangement in SC-CO_2 found that the ratio of products arising from in-cage reaction of the geminate radical pair to products arising from cage escape was invariant with pressure except near the critical point.[12] An enhanced yield of the in-cage product near P_c was attributed to solute−solvent clustering.

Scheme 1



For thermal processes, quantitative data pertaining to the effect of SCF solvents on the behavior of geminate caged pairs is sparse. Leffler suggested that for the decomposition of phenyl azo triphenylmethane (PAT), recombination of $PhN{=}N^{\bullet}$ and $^{\bullet}CPh_3$ was unimportant in SC-CO_2.[13] DeSimone found increased efficiency for radical production in the decomposition of azoisobutyronitrile (AIBN) in SCF solvent.[14] Significant cage effects were observed in the pyrolysis of benzyl phenyl ether in SC-toluene.[15]

The chlorine atom cage effect,[16] first discovered in 1983,[17] has been the subject of numerous investigations.[18−20] Put briefly, for the chlorine atom abstraction step in the free radical chlorination of an alkane (RH_2), the geminate $RHCl/Cl^{\bullet}$ caged-pair is partitioned between three pathways (Scheme 1): diffusion apart (k_{diff}), abstraction of hydrogen from RH_2 comprising the cage walls (k_{RH_2}), and a second *in-cage* abstraction of hydrogen from the alkyl chloride (k_{RHCl}). While the k_{diff} and k_{RH_2} steps result in the formation of monochloride (RHCl), the k_{RHCl} step results in the formation of polychlorides via $RCl^{\bullet} + Cl_2 \rightarrow RCl_2 + Cl^{\bullet}$. In conventional solvents, the ratio of mono- to polychlorinated products (M/P) has been shown to depend on solvent viscosity.[20] Consequently, we reasoned that the chlorine atom cage effect would be a highly sensitive probe for cage effects in supercritical fluid solvent and began an investigation of the chlorine atom cage effect in SC-CO_2 with parallel experiments in conventional solvents.

The photoinitiated free radical chlorination of cyclohexane was examined in several conventional solvents and in SC-CO_2.

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S0002-7863(96)02417-1 CCC: $12.00

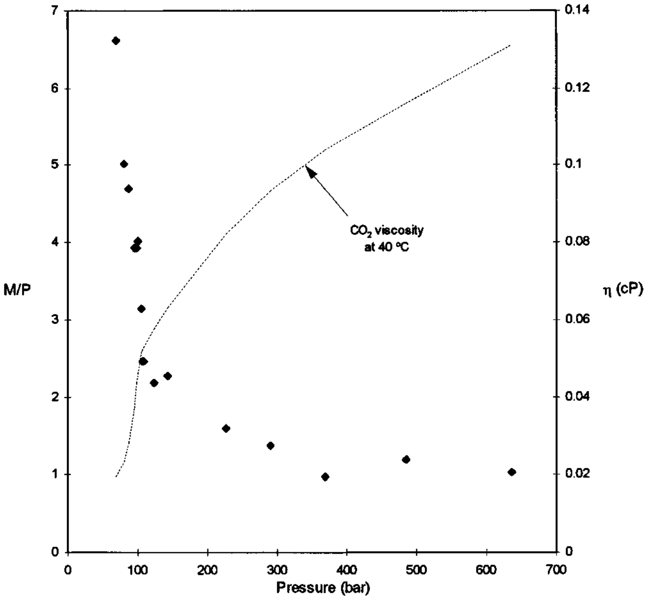

Figure 1. Ratio of mono- to polychlorides produced in the free radical chlorination of cyclohexane in supercritical carbon dioxide solvent as a function of pressure at 40 °C. (KEY: M/P ratio (◆); viscosity of SC-CO_2 (− −)).

For all these experiments, the temperature was 40 °C, the concentration of cyclohexane was 0.03 M, and the initial ratio of reactants (cyclohexane:Cl_2) was 7:1. In SC-CO_2, the M/P ratio was found to vary dramatically as a function of pressure (Figure 1),[21] especially at pressures approaching P_c. Because M/P is found to increase at lower CO_2 pressures and polychlorides are produced from in-cage reaction of the geminate RHCl/$Cl^\bullet$ caged-pair, these results suggest that the cage effect becomes *less important* near the critical point (i.e., no enhanced cage effect is observed).[22]

Cage effects are typically quantitated in terms of the Noyes model,[23] which predicts that the efficiency of cage escape should vary linearly with the inverse of viscosity ($1/\eta$). In Figure 2, the M/P ratio is plotted as a function of $1/\eta$ for the experiments conducted in SC-CO_2 *and* in conventional solvents. Overall, the plot is linear over a range of viscosities spanning 1.7 orders of magnitude (from conventional solvents to SC-CO_2). It is also worth noting that although they represent a relative small portion of the data in Figure 2, *the best straight line through the solution phase results successfully predicts the SCF phase results.*

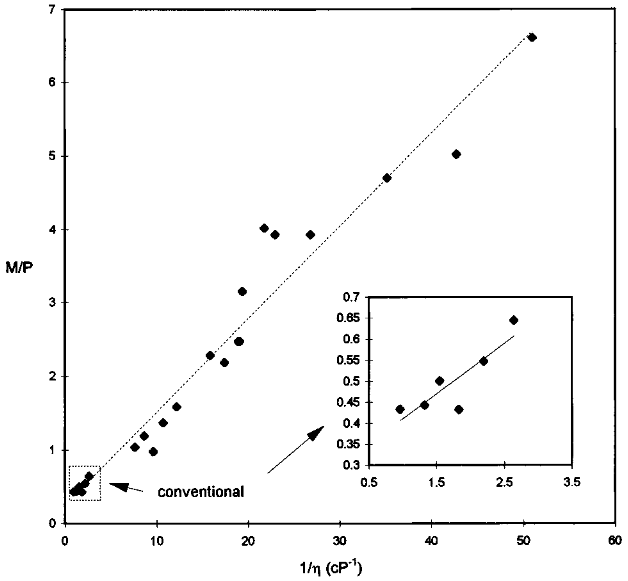

Figure 2. Ratio of mono- to polychlorides produced in the free radical chlorination of cyclohexane in conventional and supercritical fluid solvents as a function of inverse viscosity (40 °C).

Based upon these observations, we find no indication of an enhanced cage effect near the critical point in SC-CO_2 solvent. The magnitude of the cage effect observed in SC-CO_2 at all pressures examined is well within what is anticipated based upon extrapolations from conventional solvents. We thus conclude that although some studies have revealed enhanced cage effects attributable to clustering, this enhancement is unique to the specific reactions studied. In contrast to comparable reactions in conventional solvents, high yields of monochlorinated compounds may be obtained in SC-CO_2, clearly demonstrating the utility of SC-CO_2 as an excellent reaction medium for conducting free radical chlorinations.

Acknowledgment. Financial support from the National Science Foundation (CHE-9524986) is acknowledged and appreciated.

Supporting Information Available: Experimental section, details regarding solution viscosities at 40 °C, and a listing of M/P ratios for chlorination of cyclohexane in conventional solvents and SC-CO_2 (4 pages). See any current masthead page for ordering and Internet access instructions.

JA9624174

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