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## Free Radical Chlorination of Alkanes in Supercritical Carbon Dioxide: The Chlorine Atom Cage Effect as a Probe for Enhanced Cage Effects in Supercritical Fluid Solvents

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**Abstract:** The chlorine atom cage effect was used as a highly sensitive probe for studying the effect of viscosity and the possible role of solvent clusters on cage lifetimes and reactivity for reactions carried out in supercritical fluid solvents. These experiments were conducted in supercritical carbon dioxide (SC-CO<sub>2</sub>, 40 °C, at various pressures) with parallel experiments in conventional solvents and in the gas phase. The results of these experiments provide no indication of an enhanced cage effect near the critical point in SC-CO<sub>2</sub> solvent. The magnitude of the cage effect observed in SC-CO<sub>2</sub> at all pressures examined is well within what is anticipated on the basis of extrapolations from conventional solvents.

### Introduction

The supercritical state is achieved when a substance is taken above its critical temperature and pressure. The bulk properties of a supercritical fluid (SCF) are intermediate between those of a gas and a liquid. Important solvent properties of SCF's (e.g., dielectric constant, solubility parameter, and viscosity) can be altered by manipulation of temperature and pressure,<sup>1,2</sup> providing a potential means to control the behavior (kinetics) of some chemical reactions.<sup>3-6</sup>

Moreover, because of the unique nature of SCF's, there may be *additional* factors which influence chemical reactivity in a manner not possible in "conventional" solvents. Several studies have demonstrated that, for SCF's as solvents, the *local solvent density* about a solute is often enhanced at pressures just above the critical pressure (solvent/solute "clustering")<sup>7-18</sup> and that cluster formation may influence chemical reactivity.<sup>19-25</sup> Increased solvent density (and implicitly increased viscosity) may

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of polychlorides via  $\text{RCl}\cdot + \text{Cl}_2 \rightarrow \text{RCl}_2 + \text{Cl}\cdot$ . Employing the steady-state approximation (*i.e.*,  $d[(\text{RHCl}/\text{Cl}\cdot)_{\text{cage}}]/dt = 0$ ), the ratio of mono- to polychlorides can be expressed in terms of the rate constants assigned in Scheme 2 (eq 1).

$$\frac{M}{P} = \frac{k_{\text{diff}} + k_{\text{RH}_2}[\text{RH}_2]_{\text{cage walls}}}{k_{\text{RHCl}}} \quad (1)$$

Tanner has shown that in conventional solvents, the ratio of mono- to polychlorinated products (M/P) depends on solvent viscosity.<sup>44</sup> On this basis, we reasoned that the chlorine atom cage effect would be a highly sensitive probe for studying the effect of SCF viscosity and the possible role of solvent clusters on cage lifetimes and reactivity.<sup>30</sup> Toward this end, the ratio of mono- to polychlorides produced in the free radical chlorinations of cyclohexane, neopentane, and 2,3-dimethylbutane were examined in SC-CO<sub>2</sub> (40 °C at various pressures), with parallel experiments in conventional solvents. Alkane concentrations were  $\leq 0.03$  M for all these experiments, and under these conditions,  $k_{\text{RH}_2}[\text{RH}_2]_{\text{cage walls}} \ll k_{\text{diff}}$  (*i.e.*, ensuring that diffusion of RHCl and Cl $\cdot$  apart, rather than reaction of Cl $\cdot$  with RH<sub>2</sub> comprising the cage walls, was the major source of monochloride). The results are summarized in the Supporting Information (Tables S1, S2, and S4).

Cage effects are typically quantified in terms of the Noyes model. Koenig and Fischer<sup>45</sup> derived a general expression based upon the Noyes model (eq 2), where  $F = (1/\text{cage efficiency})$

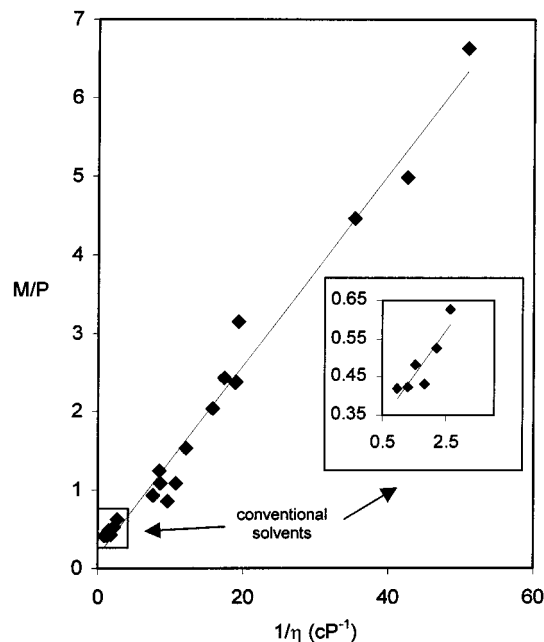
$$F = \frac{R_0 - 2b}{2b} + \frac{R_0}{2b} \left[ \frac{A_T + \alpha A_E (1/\eta)}{\alpha} + \frac{A_T A_E (1/\eta)^2}{\alpha} \right] \quad (2)$$

– 1,  $R_0$  is the separation between the two reactive components of the caged pair,  $\alpha$  is the probability (per collision) that the components will react, and  $\eta$  is 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.<sup>45</sup>

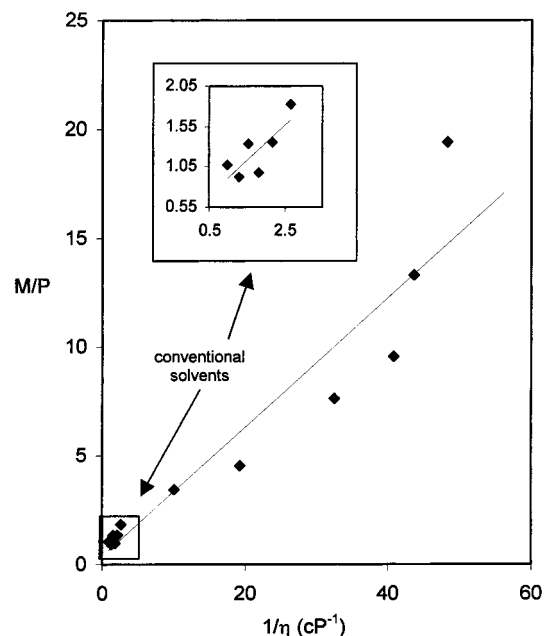
Equation 2 predicts that  $F$  will vary linearly with  $1/\eta$ , except perhaps at low viscosities, where upward curvature may be observed if  $1/\eta^2$  becomes important. Cage efficiency represents the fraction of reaction that occurs within the cage and applied to Scheme 2, is equal to  $k_{\text{RHCl}}/(k_{\text{diff}} + k_{\text{RHCl}} + k_{\text{RH}_2}[\text{RH}_2])$ . Because the mono- to polychloride ratio ( $M/P = k_{\text{diff}}/k_{\text{RHCl}}$  at the low concentrations of alkane employed,  $k_{\text{RH}_2}[\text{RH}_2] \ll k_{\text{diff}}$ ,  $k_{\text{RHCl}}$ ), it is trivial to show that  $M/P$  is also equal to  $F$ . Thus, on the basis of the Noyes model, it is anticipated that  $M/P$  will vary linearly with inverse viscosity ( $1/\eta$ ).

In Figures 1–3,  $M/P$  ratios observed in the chlorination of 2,3-dimethylbutane, neopentane, and cyclohexane are plotted as a function of  $1/\eta$  for the experiments conducted in SC-CO<sub>2</sub> and in conventional solvents. Within experimental error, these plots are linear over a range of viscosities spanning nearly 2 orders of magnitude (from conventional solvents to SC-CO<sub>2</sub>). It is also worth noting that although they represent a relative small portion of the data, *the best straight line through the solution phase results successfully predicts the SCF phase results*.

On the basis of these observations, we find no indication of an enhanced cage effect near the critical point in SC-CO<sub>2</sub> solvent, which could be attributed to solvent/solute clustering. The magnitude of the cage effect observed in SC-CO<sub>2</sub> at all



**Figure 1.** Viscosity dependence of the ratio of mono- to polychlorides (M/P) produced in the free radical chlorination of cyclohexane (conventional and SC-CO<sub>2</sub> solvent) as a function of inverse viscosity at 40 °C.



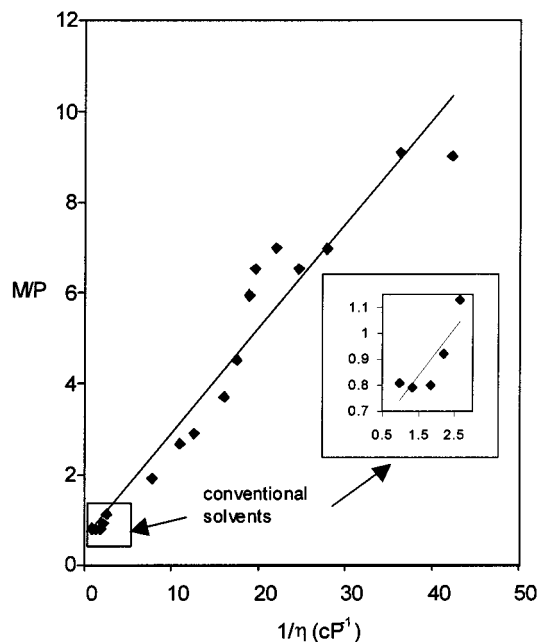
**Figure 2.** Viscosity dependence of the ratio of mono- to polychlorides (M/P) produced in the free radical chlorination of neopentane (conventional and SC-CO<sub>2</sub> solvent) as a function of inverse viscosity at 40 °C.

pressures examined is well within what is anticipated on the basis of extrapolations from conventional solvents.

**B. Reaction Selectivity in SC-CO<sub>2</sub> Compared to Conventional Solvents and the Gas Phase.** The experiments with 2,3-dimethylbutane (23DMB) provide insight into the extent that Cl $\cdot$  selectivity varies as a function of pressure in SC-CO<sub>2</sub>. In the gas phase at 40 °C, chlorine atom selectivity (*per hydrogen*) for the 3° vs 1° hydrogens of 23DMB ( $S(3^\circ/1^\circ)$ ) is 3.97.<sup>46</sup> In the condensed phase (neat 23DMB),  $S(3^\circ/1^\circ) = 3.08$  (40 °C). In SC-CO<sub>2</sub> at 40 °C, the observed selectivity ( $S(3^\circ/1^\circ)_{\text{obsd}}$ ) varies with pressure.

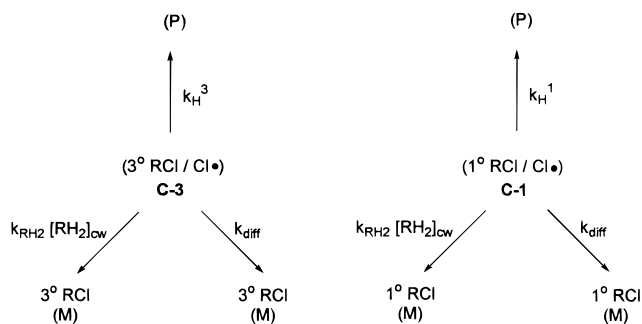
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(46)  $S(3^\circ/1^\circ) = (\text{yield of } 3^\circ \text{ RCl}/\text{yield of } 1^\circ \text{ RCl}) \times 6$ .



**Figure 3.** Viscosity dependence of the ratio of mono- to polychlorides (M/P) produced in the free radical chlorination of 2,3-dimethylbutane (conventional and SC-CO<sub>2</sub> solvent) as a function of inverse viscosity at 40 °C.

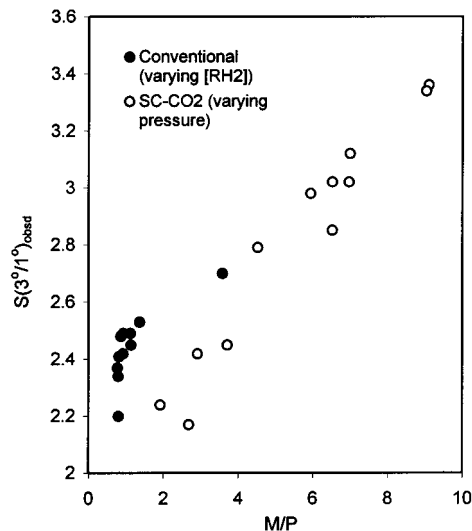
### Scheme 3



In SC-CO<sub>2</sub>, however,  $S(3^\circ/1^\circ)_{\text{obsd}}$  derived from the relative yields of 3° vs 1° RCl are not a true measure of chlorine atom selectivity because, at higher pressures, product yields are distorted by the cage effect. This point is illustrated in Scheme 3. For the chlorination of 23DMB, there are two types of caged pairs produced, 3° RCl/Cl• and 1° RCl/Cl• (designated as C-3 and C-1, respectively), and in-cage hydrogen abstraction by Cl• likely occurs at different rates for these two caged pairs (i.e.,  $k_H^3 \neq k_H^1$ ).

This distortion of the observed selectivity by the cage effect is readily demonstrated by examining the free radical chlorination of 23DMB in a conventional solvent (1,1,2-trichlorotrifluoroethane, Freon 113) at various concentrations of 23DMB. In accordance with earlier published results and eq 1, M/P was found to vary with [23DMB], and in addition, the observed selectivity as measured by the relative yields of the two monochlorides also varies. In Figure 4,  $S(3^\circ/1^\circ)_{\text{obsd}}$  is plotted against the M/P ratio for reactions conducted in both Freon 113 and SC-CO<sub>2</sub>. At high values of M/P (i.e., when the cage effect becomes relatively unimportant and the observed selectivity is expected to reflect the true selectivity), selectivity is slightly higher in SC-CO<sub>2</sub> compared to a conventional solvent.

To extract the “true”  $S(3^\circ/1^\circ)$ , the data obtained in conventional solvents were used to “correct” for the cage effect in SC-CO<sub>2</sub>. In accordance with Scheme 3, the fraction of 3° and 1°



**Figure 4.** Observed selectivity in the chlorination of 2,3-dimethylbutane (conventional and SC-CO<sub>2</sub> solvent) at 40 °C as a function of the ratio of mono- to polychlorides (M/P) produced.

RCl/Cl• caged pairs which escape ( $F_3$  and  $F_1$ , respectively) can be expressed by eqs 3 and 4 (where  $k_{\text{esc}} = k_{\text{RH}_2}[\text{RH}_2]_{\text{cw}} + k_{\text{diff}}$ ).

$$F_3 = \frac{k_{\text{esc}}}{k_{\text{esc}} + k_H^3} \quad (3)$$

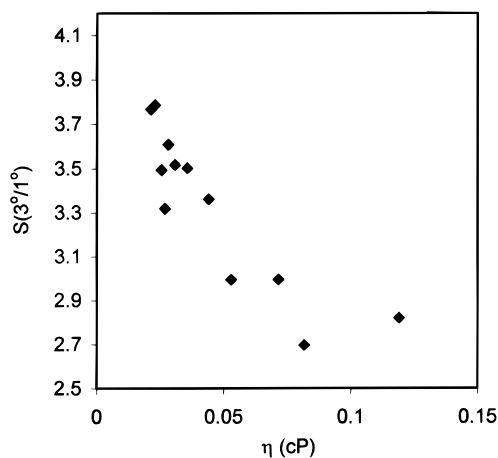
$$F_1 = \frac{k_{\text{esc}}}{k_{\text{esc}} + k_H^1} \quad (4)$$

Because the observed yields of 3° vs 1° RCl =  $(F_3/F_1)(k_3/k_1)$  (where  $k_3/k_1$  represents the true selectivity on a per molecule basis), an expression can be derived which relates M/P to  $k_3/k_1$  (eq 5).

$$\frac{M}{P} = \frac{(k_1/k_3)F_1 + F_3}{(k_1/k_3)(1 - F_1) + (1 - F_3)} \quad (5)$$

Assuming that  $k_3/k_1$  in Freon 113 and neat 23DMB is the same,  $F_1$  and  $F_3$  can be derived as a function of M/P for reactions in conventional solvents (Supporting Information, Figure S-1). Finally, assuming that the same relationship between  $F_1$  or  $F_3$  and M/P holds true in SC-CO<sub>2</sub> (i.e., assuming that the relationship between M/P and the fraction of cage escape is the same regardless of whether cage escape occurs via reaction of Cl• with the cage walls [ $k_{\text{RH}_2}$ ] or via diffusion of Cl• out of the cage, [ $k_{\text{diff}}$ ]), the data obtained in SC-CO<sub>2</sub> can be corrected for the cage effect (Figure 5).

As Figure 5 reveals, in SC-CO<sub>2</sub>  $S(3^\circ/1^\circ)$  varies as a function of viscosity between the gas- and condensed-phase values. This variation in  $S(3^\circ/1^\circ)$  can be explained as follows: The rate constants for 1°, 2°, or 3° hydrogen abstractions by Cl• from alkanes are nearly diffusion-controlled in conventional solvents. Consequently, the intrinsic selectivity of Cl• is diminished in conventional solvents because of the onset of diffusion-control. In the gas phase, selectivity is slightly higher because the barrier imposed by diffusion is eliminated. The viscosity of a supercritical fluid (a) lies between those of conventional fluid solvent and the gas phase and (b) varies with pressure. Because of the low viscosity of supercritical fluids, bimolecular rate constants greater than the  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  diffusion-controlled limit can be realized in an SCF, and as a consequence, enhanced selectivity is achieved.



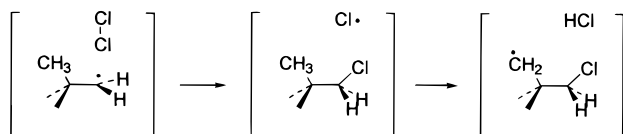
**Figure 5.** Chlorination of 2,3-dimethylbutane in SC-SO<sub>2</sub>: selectivity (corrected) as a function of viscosity.

**Table 1.** Free Radical Chlorination of Propane in SC-CO<sub>2</sub>

pressure (psi)	viscosity (cP)	S(2°/1°) <sup>a</sup>
1160	0.029	2.94 ± 0.29
1310	0.042	2.86 ± 0.29
1753	0.052	2.70 ± 0.27

<sup>a</sup> S(2°/1°) = (yield of CH<sub>3</sub>CHClCH<sub>3</sub>/yield of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Cl) × 3.

#### Scheme 4

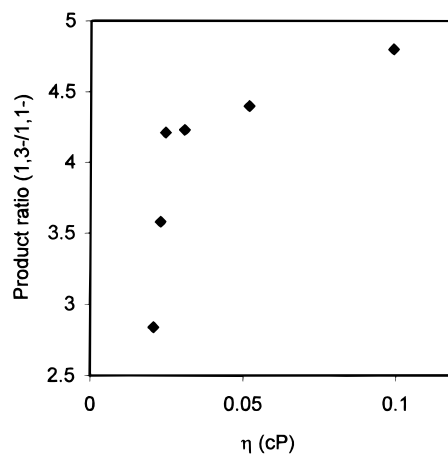


The free radical chlorination of propane in the gas phase and SC-CO<sub>2</sub> was also examined. In the gas phase at 40 °C, the chlorine atom selectivity for the 2° vs 1° hydrogens of propane ( $S(2^\circ/1^\circ)$ ) was found to be 3.09. In SC-CO<sub>2</sub>, selectivity was slightly lower (Table 1). In these experiments, *no polychlorides were detected*, which means that the relative yields of 2-chloro- vs 1-chloropropane provide an accurate assessment of  $S(2^\circ/1^\circ)$ .<sup>47</sup> While a slight variation of selectivity with pressure was noted, the differences observed were similar in magnitude to experimental error. (An extended study of the effect of pressure on M/P and  $S(2^\circ/1^\circ)$  was not pursued because, at high pressures, recovery of the volatile reaction products proved to be erratic and unreliable.)

**C. Dichloride Pattern in the Chlorination of Neopentane in SC-CO<sub>2</sub>.** Abstraction of the *second* hydrogen within the RHCl/Cl· caged pair occurs at the site(s) in close proximity to the initially abstracted hydrogen atom, and this second hydrogen abstraction occurs on a time scale competitive with molecular rotation.<sup>42,43</sup> This phenomenon is especially apparent in the chlorination of neopentane:<sup>43</sup> For the geminate neopentyl chloride/Cl· caged pair, the methyl hydrogens are in closest proximity to the initially formed chlorine atom (Scheme 4) and are abstracted more readily. Consequently, the ratio of 1,3-dichloro-2,2-dimethylpropane and 1,1-dichloro-2,2-dimethylpropane produced from the geminate caged pair is higher (on the order of (4–5):1) compared to the 1,3/1,1 ratio produced from a diffusive caged pair (ca. 2.2:1, based upon the chlorination of neopentyl chloride),<sup>43</sup> where all possible trajectories are possible.

An analysis of the ratio of 1,3- to 1,1- dichlorides formed from the chlorination of neopentane in SC-CO<sub>2</sub> affords at least

(4)  $S(2^\circ/1^\circ)$  = (yield of 2° RCl/yield of 1° RCl) × 3.



**Figure 6.** Product ratio (1,3- to 1,1-dichloro-2,2-dimethylpropane) formed in the chlorination of neopentane in SC-CO<sub>2</sub> solvent as a function of viscosity (40 °C).

a qualitative description of viscosity effects on molecular rotation. At 40 °C, the gas-phase chlorination of neopentane produces 1,3- and 1,1-dichloro-2,2-dimethylpropane in a 2.42:1 ratio. Because there is no cage effect in the gas phase, this ratio represents the selectivity associated with the abstraction of hydrogen from neopentyl chloride by Cl· via a diffusive encounter.

In SC-CO<sub>2</sub>, the ratio of the dichlorides varies with pressure. In Figure 6, the dichloride ratio is plotted as a function of viscosity. At high viscosities, the 1,3-isomer dominates because of the cage effect. At low viscosities, the dichloride ratio decreases and approaches the gas-phase value, suggesting (at low viscosities) dichloride formation occurs predominantly from diffusive encounters and not the cage effect.

#### Conclusions

In SC-CO<sub>2</sub>, the magnitude of the chlorine atom cage effect is as anticipated on the basis of extrapolations from conventional solvents. No evidence was found for an *enhanced* cage effect in SC-CO<sub>2</sub>, which might be attributable to solvent/solute clustering. Chlorine atom selectivities in SC-CO<sub>2</sub> vary slightly with pressure (viscosity) and are intermediate between gas- and solution-phase values. Compared to that of conventional liquid solvents, the higher selectivity observed in SC-CO<sub>2</sub> is attributable to the low viscosity of the SCF media, which allows absolute rate constants to exceed the 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> limit imposed by the viscosity of conventional solvents. Finally, these results demonstrate that the “tunable” solvent properties of a supercritical fluid provide a means of controlling reactivity and selectivity. Thus, considering its properties as a reaction solvent and the fact that it offers a nontoxic and less environmentally threatening alternative to conventional solvents, SC-CO<sub>2</sub> emerges an excellent solvent for radical reactions.

#### Experimental Section

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

**Materials.** CFCl<sub>3</sub>, CF<sub>2</sub>ClCCl<sub>2</sub>F, decane (Aldrich), and CFCl<sub>2</sub>CFCl<sub>2</sub> (PCR Inc.) were used as received. Cyclohexane (Aldrich or Matheson)

and 2,3-dimethylbutane were washed with dilute sulfuric acid, neutralized with saturated sodium bicarbonate, dried over magnesium sulfate, and distilled. Neopentane (Wiley Organics) was purified by treatment with Br<sub>2</sub> and distilled. SFC grade carbon dioxide was obtained from Scott Specialty Gases.

**Gas-Phase Chlorination.** For 2,3-dimethylbutane and cyclohexane, the appropriate volume of alkane was added to a large pressure tube (ca. 180 mL in volume). Typically, a 7:1 ratio of alkane to Cl<sub>2</sub> was used. The pressure tube was subsequently degassed by performing three or four freeze–pump–thaw cycles. Neopentane or propane was measured manometrically and condensed into the pressure tube via a vacuum line. Cl<sub>2</sub> was measured with a calibrated gas pipet and purified immediately before use by condensation from a trap at –78 °C directly into the degassed pressure tube. The pressure tube was sealed and wrapped in aluminum foil, and its contents were allowed to equilibrate to 40 °C in the dark in a thermostatically maintained water bath. After the foil was removed, the pressure tube was irradiated for 20 min by a 150 W tungsten lamp. Afterward, the pressure tube was cooled in liquid nitrogen, the products were collected in either hexanes or decane, and the internal standard was added. The reaction mixture was analyzed directly by GLC in triplicate.

**Solution-Phase Chlorination.** All solution-phase reactions were conducted in approximately 16 mL of solvent. The solvent was placed in a ca. 35 mL Pyrex pressure tube, the alkane was added as described above, and the mixture was degassed three or four times by the freeze–pump–thaw method. Chlorine was added as described above, the pressure tube was wrapped in aluminum foil, and its contents were allowed to equilibrate to 40 °C. During illumination, the gas phase occupied by the dead space volume of the pressure tube was shielded from light. After illumination for 20 min, the pressure tube was cooled to room temperature, the internal standard was added, and the reaction mixture was analyzed by GLC in triplicate.

**Supercritical CO<sub>2</sub> Chlorination.** The details regarding the apparatus for the chlorination of cyclohexane in supercritical carbon dioxide have been previously reported.<sup>36</sup> Briefly, the reactor is constructed of Hastelloy C-276 and is equipped with a sapphire window (for irradiation) and a magnetic stir bar. For liquid substrates (cyclohexane and 2,3-dimethylbutane), the typical procedure follows: The appropriate volume of alkane was placed in a 1 mL ampule. The ampule was degassed by the freeze–pump–thaw method, sealed under

vacuum, and placed in the reactor. A second ampule containing the appropriate amount of Cl<sub>2</sub> was added to the reactor (approximately 16 mL in volume). The reactor was then sealed, covered with aluminum foil, and brought to 40 °C. Following several argon purges, the reactor was pressurized with CO<sub>2</sub> and its contents were allowed to equilibrate at 40 °C and the desired pressure for several minutes. The aluminum foil was removed, and the reactor was illuminated as described previously. Following illumination, the contents of the reactor were bubbled slowly into hexanes cooled to 0 °C. The internal standard was added, and direct analyses by GLC were performed in triplicate. Reactions involving neopentane were conducted in the same manner, with the neopentane being measured manometrically and condensed into the degassed ampule. Due to its volatility, propane could not be sealed in an ampule and was added directly to the reactor. The reactor was purged several times with propane and sealed at ambient pressure. The propane:Cl<sub>2</sub> ratio for these reactions was approximately 14:1. Following illumination, the products were collected in hexane cooled to dry ice/acetone temperatures (–78 °C).

*Note!* Because of the hazards associated with high-pressure work, we were especially careful to ensure that the pressures utilized in this study did not exceed the specifications of our system (ca. 15 000 psi). The Hastelloy reactor (the details of which are provided in ref 36) has proven especially suitable for reactions involving corrosive materials such as Cl<sub>2</sub> and Br<sub>2</sub>; after several years of use, there are no visible signs of corrosion.

**Acknowledgment.** Financial support from the National Science Foundation (Grant CHE-9524986) is acknowledged and appreciated. This paper is dedicated to Prof. Glen A. Russell (1925–1998).

**Supporting Information Available:** Tables of experimental results pertaining to the chlorination of cyclohexane, neopentane, and 2,3-dimethylbutane and a narrative detailing the procedure for obtaining corrected values of  $S(3^\circ/1^\circ)$  in SC-CO<sub>2</sub> solvent (8 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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