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# Solvent cage effects. I. Effect of radical mass and size on radical cage pair recombination efficiency. II. Is geminate recombination of polar radicals sensitive to solvent polarity?

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Dedicated to Arthur W. Adamson on the occasion of his 80th birthday

## Contents

## Abstract

The radical cage effect is briefly reviewed with an emphasis on how radical mass and size affect the cage recombination efficiencies ($F_{cP}$) of radical cage pairs. The results of one study show that $F_{cP}^{-1}$ varies linearly with radical radius$^{-2}$ and radical mass$^{1/2}$, but additional studies are needed to determine if this result is general. The results of a new study on solvent polarity effects are also presented. The effect of solvent polarity on the geminate recombination of polar $Cp'Mo(CO)_3$ ($Cp' = \eta^5$-$C_5H_4CH_3$) radical cage pairs was studied by using a

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series of solvent systems that ranged from nonpolar to polar. The solvent systems consisted of a solvent and a viscogen of similar polarity. The solvents were hexane–squalane, hexane–paraffin oil, glyme–polyglyme, THF–polyglyme, and ethanol–propylene glycol. The cage effects were identical in four of the five solvent systems (hexane–paraffin oil is the exception), and no trend with solvent polarity was observed. From these results, it is concluded that the influence of solvent polarity is either weak or absent altogether. A similar analysis of the data of Szwarc et al. (*J. Am. Chem. Soc.* 90 (1968) 278) for [$H_3C^\bullet$, ${}^\bullet CH_3$] and [$F_3C^\bullet$, ${}^\bullet CF_3$] cage pairs showed that, although there is a solvent effect, it cannot be attributed to solvent polarity. All of these results are consistent with a model for the cage effect in which geminate recombination of the $Cp'Mo(CO)_3$ radicals is faster than molecular rotation. Rotational correlation times and diffusion coefficients were measured in the solvents used herein and the results support the model.

*Keywords:* Solvent cage effects; Radical cage pair recombination; Polar radicals; Solvent polarity

## 1. Introduction

The concept of the ‘cage effect’ was introduced by Franck and Rabinowitch [1–3] in 1934 to explain why the efficiency of $I_2$ photodissociation was lower in solution than in the gas phase. It was proposed that the solvent temporarily encapsulates the reactive $I^\bullet$ atoms in a ‘solvent cage’, causing them to remain as colliding neighbors before they either recombine or diffuse apart. This concept is illustrated for a general homolysis reaction in Eq. (1).

$$\mathrm{R{-}R} \underset{k_c}{\overset{k_1 \text{ or } h\nu}{\rightleftharpoons}} \underset{\text{cage pair}}{(\mathrm{R}^\bullet, {}^\bullet\mathrm{R})} \underset{k_D}{\overset{k_d}{\rightleftharpoons}} \underset{\text{free radicals}}{2\mathrm{R}^\bullet} \rightarrow \text{Products} \tag{1}$$

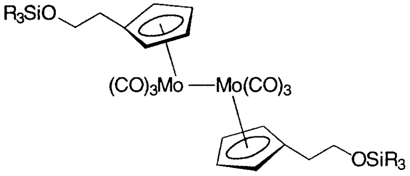
For quantitative discussions, the ‘cage recombination efficiency’ (denoted as $F_c$ and commonly called the ‘cage effect’) is defined as the ratio of the rate constant for cage recombination ($k_c$) to the sum of the rate constants for all cage processes. In the reaction above, $F_c = k_c/(k_c + k_d)$ [4]. $F_c$ for a photochemically formed cage pair does not necessarily equal $F_c$ for the same cage pair formed by thermolysis or by diffusional collision of two free radicals [5,6]. In order to differentiate these cases, the photochemical cage efficiency will be denoted $F_{cP}$ in this paper and the associated rate constants as $k_{cP}$ and $k_{dP}$.

Cage effects have an enormous impact on both photochemical and thermal reactivity in solution [7]. In particular, they are necessary to explain a host of kinetic observations and fundamental reaction phenomena. For example, cage effects are necessary to explain magnetic isotope [8–12] and CIDNP [13–18] effects, rate-viscosity correlations [19–21], variations in products and yields as a function of medium [22–25], and variations in quantum yields as a function of medium [26–48].

Despite the recognition that cage effects are important, there is practically no predictive knowledge of the cage effect because virtually nothing systematic or quantitative is known about how changes in radical parameters such as size, shape, mass, etc., affect the cage effect [49]. For that reason, we began a research program to investigate the effect of various radical and solvent structural parameters on the cage effect. Selected results are reviewed below and then a new photochemical study investigating the effect of solvent polarity on the cage effect is reported.

## 2. Radical mass and size effects

Radical cage pairs with radicals of different size and mass were generated by photolysis of the metal–metal bonds in molecules **1**–**1**–**4**–**4** [49].

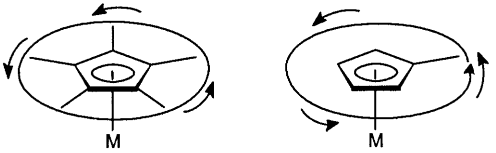


**1-1**, R = Me; **2-2**, R = *i*-Pr; **3-3**, R = *n*-Pr;
**4-4**, R = *n*-Hx; **5-5** has MeCp ligands

The $F_{cP}$ values for the resultant cage pairs are shown in Fig. 1 as a function of viscosity. (Our method for measuring $F_{cP}$ is discussed in more detail below. Also see [49]). Note that the cage effect increases with increasing length of the substituent on the Cp ligand ([**1**$^\bullet$, $^\bullet$**1**] < [**2**$^\bullet$, $^\bullet$**2**] ≤ [**3**$^\bullet$, $^\bullet$**3**] < [**4**$^\bullet$, $^\bullet$**4**]). In order to quantify these results, the results were compared to Noyes's cage effect model [26,50–53]. In his mathematical description of the cage effect, Noyes predicted that the cage effect will increase as radical size increases and as radical mass decreases [50–53]. The reasoning behind the increase in cage effect with decreasing radical mass is that lighter radicals will have lower momentum and will be less able to break out of the solvent cage. More specifically, he predicted that the ratio $k_{dP}/k_{cP}$ (which is equal to $(F_{cP}^{-1} - 1)$) is proportional to $m^{1/2}/r^2$, where $r$ is the radius of the radical and $m$ is the mass [6]. Plots of $(F_{cP}^{-1} - 1)$ versus $m^{1/2}/r^2$ for molecules **1**–**1**–**4**–**4** (and **5**–**5**) are shown in Fig. 2. Each line in the figure shows data for a different viscosity. Note the excellent fit of the experimental results to the prediction for molecules **1**–**1**–**4**–**4**. The points lying off the lines are for the **5**–**5** molecule. For the interesting reason discussed below, these points are expected to lie off the lines. Thus, for a series of structurally similar radical cage pairs, the ratio $k_{dP}/k_{cP}$ for these pairs varies with radius$^{-2}$ and with mass$^{1/2}$. Investigation of mass and size effects is continuing in our laboratory in order to establish the generality of this result.

## 3. Cp′ versus Cp*

The cage recombination efficiencies for the [Cp′(CO)$_3$Mo$^\bullet$, $^\bullet$Mo(CO)$_3$Cp′] and [Cp*(CO)$_3$Mo$^\bullet$, $^\bullet$Mo(CO)$_3$Cp*] (Cp′ = $\eta^5$-$C_5H_4CH_3$; Cp* = $\eta^5$-$C_5(CH_3)_5$) radical cage pairs in THF are essentially identical, despite the larger static volume of the Cp* ligand [49]. This finding is intriguing because the conclusions in the preceding section predict that the cage effect in [Cp*(CO)$_3$Mo$^\bullet$, $^\bullet$Mo(CO)$_3$Cp*] should be larger because the radicals are larger. However, the similarity in $F_{\rm cP}$ for these two cage pairs is explainable if Cp′ ring rotation is fast compared to the $k_{\rm cP}$ and $k_{\rm dP}$ processes (generally $k_{\rm rotation} \geq 10^{11}$ s$^{-1}$ [54]). When ring rotation is fast, then the effective size (i.e. dynamic volume) swept out by the rotating Cp′ ligand is equal to that of the Cp* ligand, therefore one would not expect differences in the cage effect due to static volume.



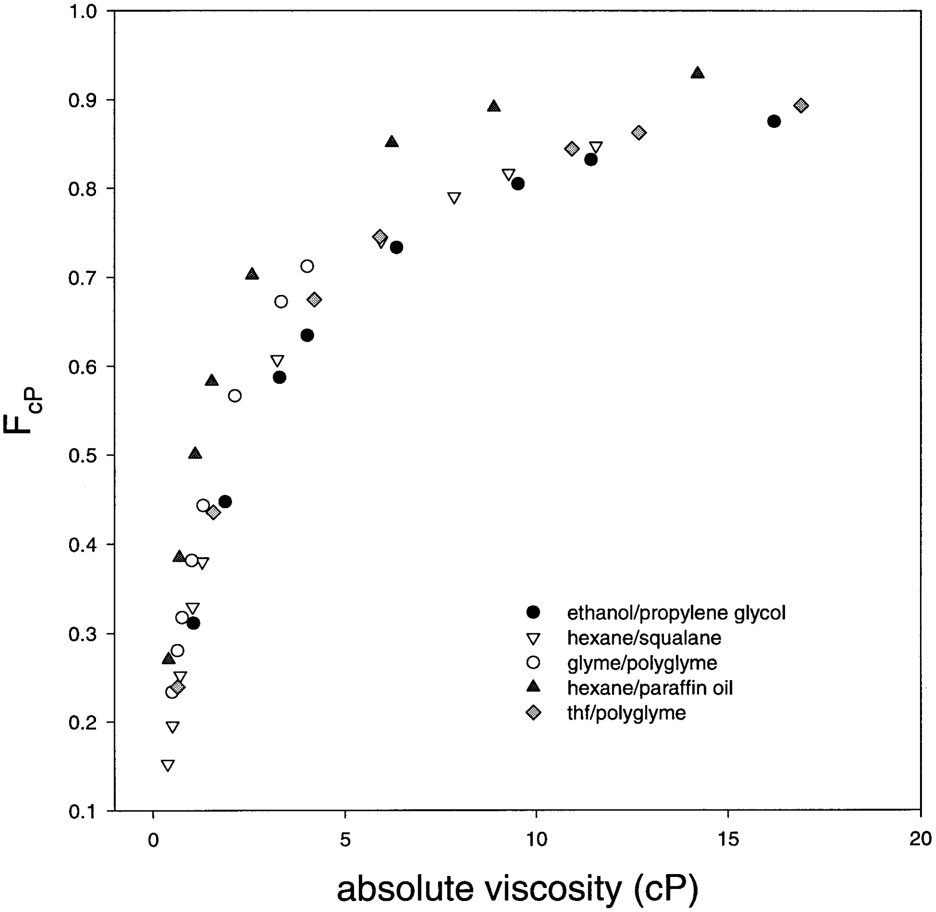


Fig. 1. Plot of $F_{\rm cP}$ vs. absolute viscosity for $(R_3SiOCH_2CH_2Cp)_2Mo_2(CO)_6$ [R = Me (●), *i*-Pr (▲), *n*-Pr (), *n*-Hx (▼)] with $CCl_4$ (2 M) at 23 ± 1°C in hexane–paraffin oil. All error bars represent $\pm 1\sigma$. Reprinted with permission from Ref. [49]. Copyright 1998 American Chemical Society.

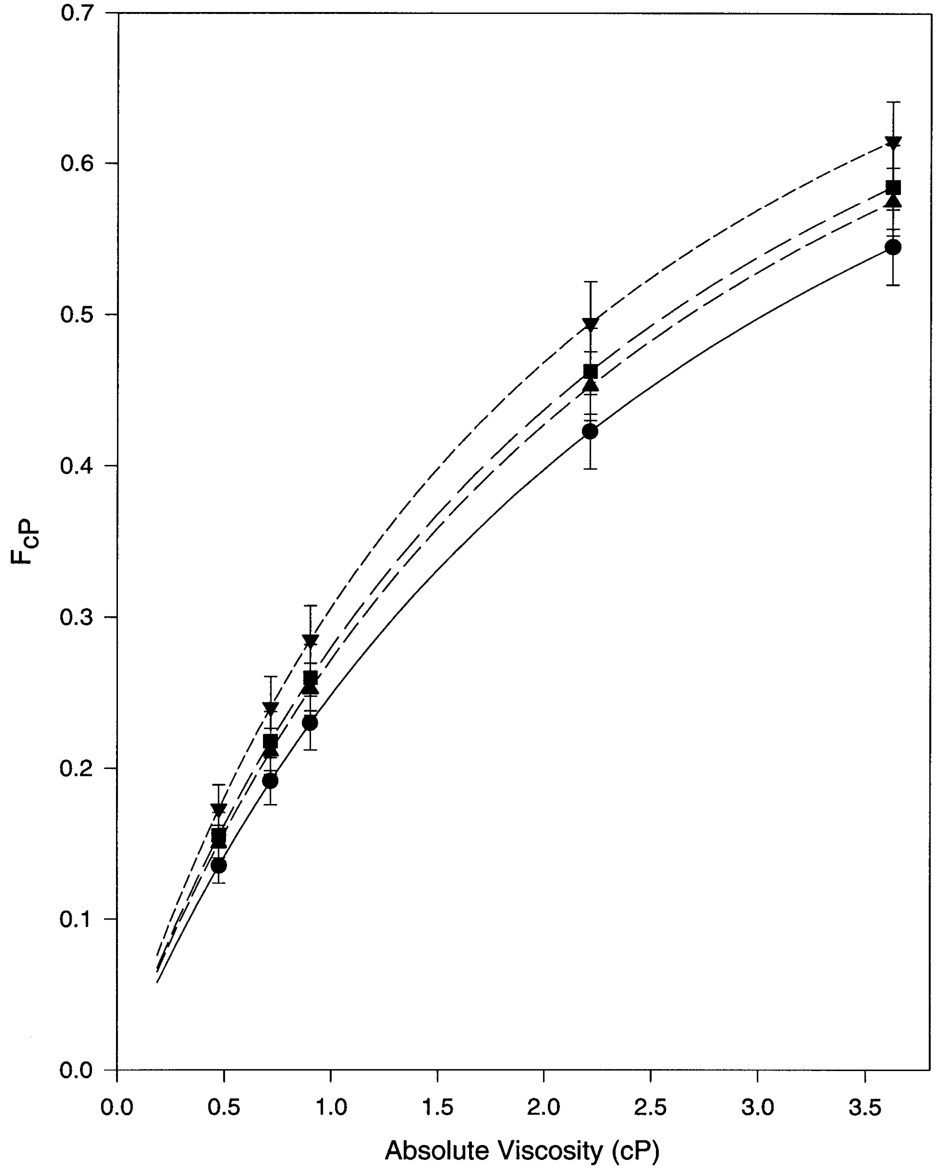


Fig. 2. Plot of $F_{cP}^{-1} - 1$ vs. $m^{1/2}/r^2$ ($m$ = mass of the radical; $r$ = the radius of a sphere with the same volume as the static volume of the radical) for $(R_3SiOCH_2CH_2Cp)_2Mo_2(CO)_6$ (R = Me, *i*-Pr, *n*-Pr, *n*-Hx) and $Cp'_2Mo_2(CO)_6$ (in this order left to right) at the measured viscosities of: 0.47 (●), 0.72 (), 0.90 (▲), 2.2 (▼), 3.6 (◆) cP. Reprinted with permission from Ref. [49]. Copyright 1998 American Chemical Society.

This explanation may also explain why the values of $k_{dP}/k_{cP}$ for [Cp′(CO)$_3$Mo$^\bullet$, $^\bullet$Mo(CO)$_3$Cp′] are somewhat lower than predicted by the lines in Fig. 2. If the Cp′ ring is rotating rapidly (the CpCH$_2$CH$_2$OSiR$_3$ rings are probably not) then ring rotation will increase the effective volume of the Cp′(CO)$_3$Mo$^\bullet$ radical (**5**$^\bullet$) and, in turn, the effective radius, which would move the points for **5**–**5** to the left and closer to the line [55]. Note, however, that time-resolved laser experiments (see below) indicate that geminate recombination occurs on the femtosecond time scale. If so, then ring rotation would not be competitive with geminate recombination. If this is the case, an alternative explanation for the similarity in cage effects for [Cp′(CO)$_3$Mo$^\bullet$, $^\bullet$Mo(CO)$_3$Cp′] and [Cp*(CO)$_3$Mo$^\bullet$, $^\bullet$Mo(CO)$_3$Cp*] is that the slight increase in mass for Cp*(CO)$_3$Mo$^\bullet$ is compensated for by the slight increase in effective radius such that $m^{1/2}/r^2$, and therefore $k_{dP}/k_{cP}$, remains the same.

## 4. Comparison of [Cp′(CO)$_3$W$^\bullet$, $^\bullet$W(CO)$_3$Cp′] with [Cp′(CO)$_3$Mo$^\bullet$, $^\bullet$Mo(CO)$_3$Cp′]

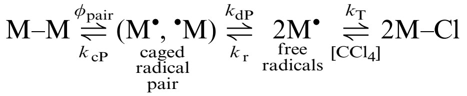
The cage effect for the [Cp′(CO)$_3$W$^\bullet$, $^\bullet$W(CO)$_3$Cp′] cage pair is larger than that of the analogous [Cp′(CO)$_3$Mo$^\bullet$, $^\bullet$Mo(CO)$_3$Cp′] cage pair, at any selected viscosity [56,57]. The obvious difference between the W- and Mo-containing radicals is the increased mass of the former (the W–L and Mo–L bond lengths are identical so there is no increase in size). Yet, the difference in $F_{cP}$ values cannot be attributed to the differences in the radicals' masses because, as the results with molecules **1**–**1**–**4**–**4** show, the larger mass for the W-containing radical should lead to a smaller cage effect. Other factors must therefore be at work. One possible factor is the smaller difference between the bond dissociation energy and the photochemical excitation energy for Cp$'_2$W$_2$(CO)$_6$ compared to Cp$'_2$Mo$_2$(CO)$_6$ [58]. The excess photonic energy in the case of Mo may lead to an increase in translational energy in the photogenerated radicals and a consequent decrease in the cage effect. Such an effect has been observed in studies with I$_2$ [5,6], but the usual assumption with multinuclear radicals is that the excess energy is rapidly dissipated to the solvent. This assumption has not been tested, however. Alternatively, the larger cage effect for the W-containing radical pair may reflect the increased driving force (and consequently lower activation barrier) for the recombination of the two Cp′(CO)$_3$W$^\bullet$ radicals compared to the Cp′(CO)$_3$Mo$^\bullet$ radicals [58]. A third explanation is the increased spin–orbit coupling in W compared to Mo. The increase will facilitate intersystem crossing, which may be important if there is a spin barrier to recombination of the cage pair. The fundamental insight to be gained from the comparison of [Cp′(CO)$_3$W$^\bullet$, $^\bullet$W(CO)$_3$Cp′] with [Cp′(CO)$_3$Mo$^\bullet$, $^\bullet$Mo(CO)$_3$Cp′] is that differences in bond energies and spin–orbit coupling may influence the cage effect.

## 5. Effect of solvent polarity on the cage effect

Viscosity is often considered to be the most important solvent characteristic that affects the recombination efficiency of geminate radical cage pairs [6,7]. However, when the radicals undergoing recombination are polar, the polarity of the solvent might also be expected to significantly affect the ratio of the rates for recombination and cage escape. The recombination efficiencies ($F_{cP}$) of a variety of radical pairs, both polar and nonpolar, have been examined in numerous studies [7], but to our knowledge, no attempt was made in any of these studies to determine the effect of solvent polarity on the cage recombination efficiencies of polar radicals. Because of our interest in the factors that influence the cage effect, we decided to investigate the effect of solvent polarity. It is shown below that solvent polarity effects are weak or absent, even when the radicals undergoing geminate recombination are polar.

As in our previous studies, the radical cage pairs used in this study were generated by the photolysis of $Cp'_2Mo_2(CO)_6$, as shown in Scheme (1) [49]. The $Cp'Mo(CO)_3$ radicals were calculated to have a dipole moment of about 3.9 D [59]. The photolyses were carried out at 23°C in solvents of increasing polarity: hexane, THF, glyme, and ethanol [60–63]. As described in the next paragraph, the $F_{cP}$ values were obtained by measuring the quantum yield of the reaction as a function of viscosity. Squalane or paraffin oil was added to the hexane solution to increase the viscosity, polyglyme (average MW = 256) was added to the glyme solution, polyglyme (average MW = 500) was added to the THF solution, and propylene glycol was added to the ethanol solution. Each viscogen was chosen to match the dielectric constant of the more fluid solvent as closely as possible, in order to avoid preferential solvation [64]. Thus, polarity is the primary difference between the solvent systems employed. Each solution also contained 20% $CCl_4$ by volume to ensure complete trapping of all radicals that escape the solvent cage. The viscosities of each solvent mixture were measured at 23°C (the same temperature at which the photolyses were carried out).

The pathway for the reaction of the metal–metal bonded dimers with $CCl_4$ is shown in Scheme (1):



$$\text{M–M} \underset{k_{cP}}{\overset{\phi_{pair}}{\rightleftharpoons}} \underset{\text{caged radical pair}}{(\text{M}^\bullet, {}^\bullet\text{M})} \underset{k_r}{\overset{k_{dP}}{\rightleftharpoons}} \underset{\text{free radicals}}{2\text{M}^\bullet} \underset{[\text{CCl}_4]}{\overset{k_T}{\rightleftharpoons}} 2\text{M–Cl}$$

M = metal containing fragment (Scheme (1))

Values of $F_{cP}$ were determined as follows. Using the definition of $F_{cP}$ and making the steady-state approximation for the concentration of caged radical pairs [65], kinetic analysis of Scheme (1) leads to the following expression for the observed quantum yield for loss of $Cp'_2Mo_2(CO)_6$, where $\phi_{pair}$ is the quantum yield for formation of the radical cage pair:

$$\Phi_{obs} = \phi_{pair}(1 - F_{cP}) \tag{2}$$

The assumption is made that the recombination process is independent of bulk viscosity and that diffusion out of the initial solvent cage follows the Stokes–Einstein–Smoluchowski relationship, $k_d \propto D \propto 1/\eta$. These assumptions lead to the following expression for $F_{cP}$:

$$F_{cP} = \frac{1}{1 + c/\eta} \tag{3}$$

where $c$ is a fitting parameter that includes $k_c$. Eqs. (2) and (3) relate the observed quantum yield to solvent viscosity. A plot of $\Phi_{obs}$ versus $\eta$ yields values for $\phi_{pair}$ and $c$, and $F_{cP}$ may then be calculated using Eq. (3).

Fig. 3 shows $F_{cP}$ as a function of viscosity [66] for the recombination of caged pairs of Cp′Mo(CO)$_3$ radicals in the five solvent systems at 23°C. Note that four of the five curves are identical. This was a somewhat surprising result because it is contrary to assumptions often made about the effects of a polar solvent on cage recombination [67]. Evidently the higher polarities of the ethereal and alcoholic solvent systems do not change the cage recombination efficiency of the polar [59] Cp′Mo(CO)$_3$ radicals from that in hexane–squalane. To further probe this conclusion, we re-examined the data of Szwarc et al. for the geminate recombination of trifluoromethyl radicals [68] and methyl radicals [69]. This data [70] is plotted in Figs. 4 and 5, respectively. Trifluoromethyl radicals are known to be pyramidal, and are thus polar [71,72], while methyl radicals are planar and nonpolar. Figs. 4 and 5 show that, although there is a solvent effect on the $F_{cP}$ values for both radicals, it is not correlated with polarity. For methyl radicals (Fig. 5), the $F_{cP}$ values obtained in benzyl benzoate (the four open circles at highest viscosity) are outliers, while the $F_{cP}$ values for chloroform, which is similar in polarity to benzyl benzoate [73], are grouped with the nonpolar solvents. For trifluoromethyl radicals (Fig. 4), the $F_{cP}$ values for the polar solvents are scattered and they bracket the data for the nonpolar solvents.

The other notable result in Fig. 3 is that although viscosity is an adequate predictor for the cage effect in most solvent systems, especially at low viscosities, the hexane–paraffin oil data do not follow the trend shown by the other solvent systems. This leads to the conclusion that although polarity does not influence, or only minimally influences the cage effect, there is a variable in addition to viscosity that may influence the rate of cage recombination. Why the hexane–paraffin oil solvent system should be significantly different from the hexane–squalane system is not readily apparent. NMR studies conducted with adamantane to determine rotational correlation times and diffusion coefficients in each solvent system gave nearly identical results for both rotation and diffusion through the solvents (see below). These results suggest that the solvent dynamics in the hexane–paraffin oil and hexane–squalane solvent systems are very similar, as would be expected.

In summary, there is no difference in the magnitude of the cage effect for the recombination of caged pairs of Cp′Mo(CO)$_3$ radicals in hydrocarbon, ethereal, and alcoholic solvents, from which it is concluded that cage recombination of polar radicals is not strongly sensitive to the polarity of the medium. Reasons for the insensitivity to solvent polarity are discussed in the next section. In some cases, the interaction between the radicals themselves might be more important than that between the radicals and the solvent. Alternatively, interactions with the solvent may also be highly localized, such that models that attempt to predict the cage effect in terms of a single bulk solvent parameter such as viscosity, internal pressure (or cohesive energy density) [74,75], or more complex parameters [76] may not be universally applicable.

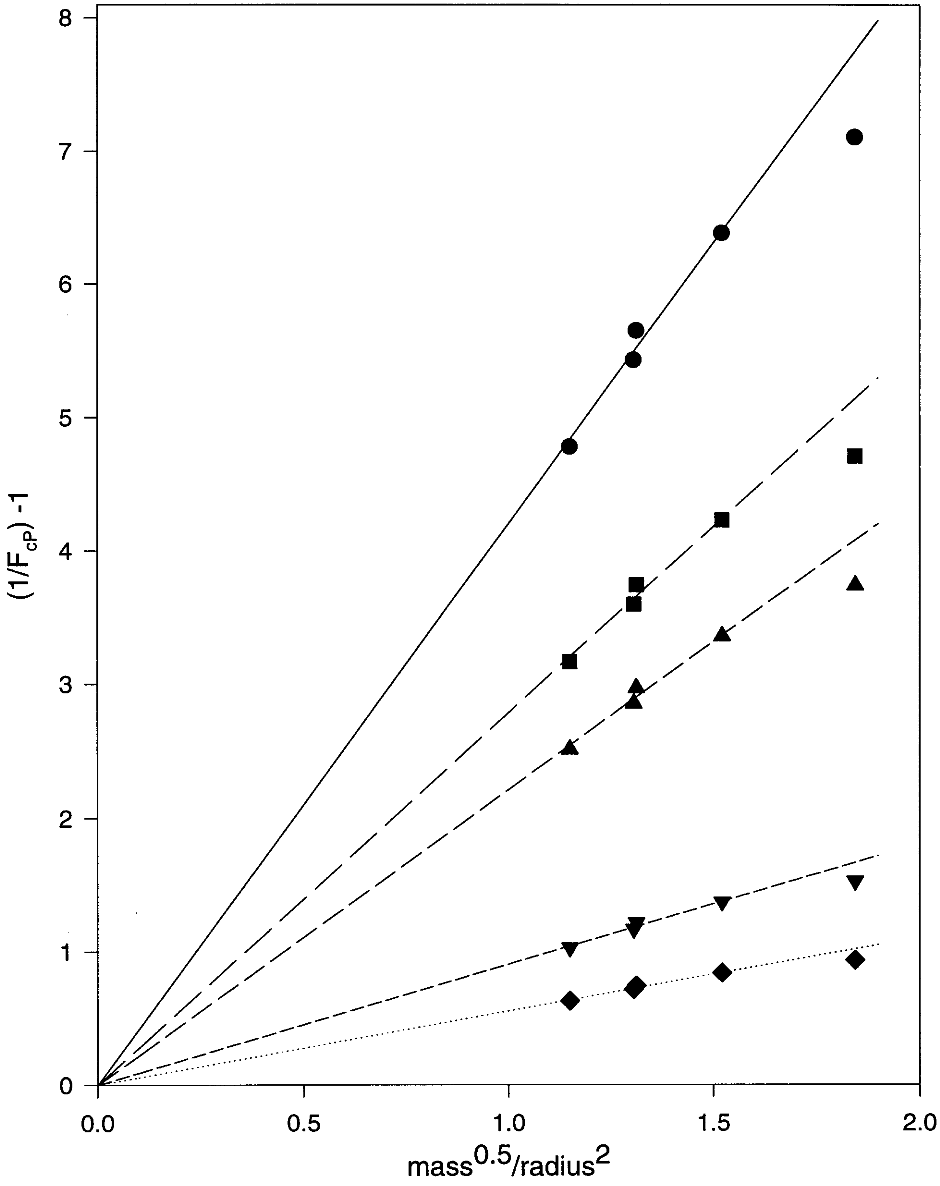


Fig. 3. Cage effect ($F_{cP}$) vs. absolute viscosity for Cp′Mo(CO)$_3$ radicals with CCl$_4$ (2 M) at 23 ± 1°C in hexane–squalane, hexane–paraffin oil, glyme–polyglyme, THF–polyglyme and ethanol–propylene glycol.

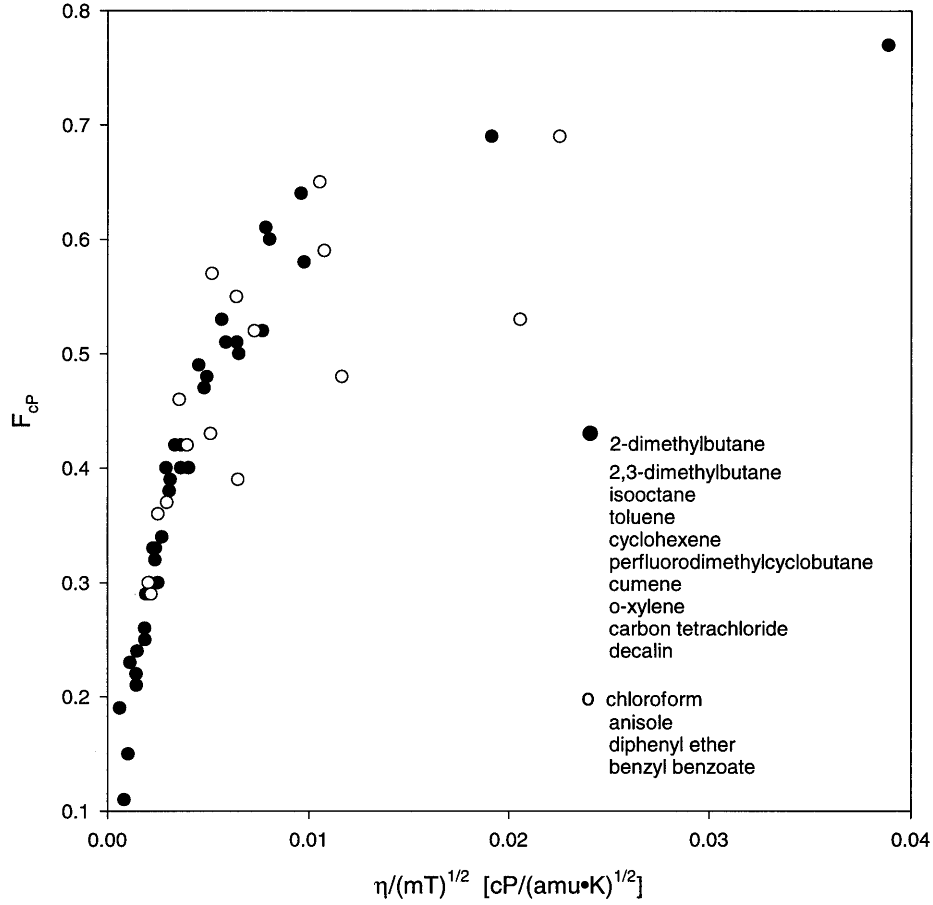


Fig. 4. Cage effect ($F_{cP}$) versus $\eta/(mT)^{1/2}$ for trifluoromethyl radicals [68] in nonpolar solvents (●) and in polar solvents (○).

## 6. The effect of spacer molecules on the cage effect

In the majority of studies on solvent cage effects, the geminate radicals were generated from azo or peroxy compounds [7]. When these molecules are thermolyzed or photolyzed, they liberate $N_2$, CO, or $CO_2$ and create a radical cage pair.

$$\text{R–N=N–R} \rightarrow (\text{R}^\bullet,\ {}^\bullet\text{R}) + \text{N}_2$$

It was always assumed that the presence of these 'spacer' molecules did not significantly affect the kinetics of geminate recombination. In other words, it was implicitly believed that the small spacer molecule would quickly diffuse out of the solvent cage. This assumption is questionable. Consider the photolysis of azomethane, perfluoroazomethane, or acetyl peroxide. In the cage pairs generated from these molecules, the radicals undergoing geminate recombination are of comparable size to the spacer molecule, and there is no reason to believe that the spacer would diffuse out of the cage any faster than the radicals themselves. Diffusion coefficients of most small neutral molecules fall in the range 0.5–5 × $10^{-5}$ $cm^2$ $s^{-1}$ [77]. In particular, the diffusion coefficients of $CH_4$, $N_2$ and $CO_2$ in water at 25°C are $1.88 \times 10^{-5}$, $2.34 \times 10^{-5}$, and $1.9 \times 10^{-5}$ $cm^2$ $s^{-1}$, respectively [77]. Geminate radicals are usually considered to be no longer in the cage as soon as a solvent molecule has come between them. Clearly this is incompatible with the use of spacers in molecules from which geminate radicals are to be generated. Thus, the effect of the free spacer molecule on the cage effect is not necessarily negligible.

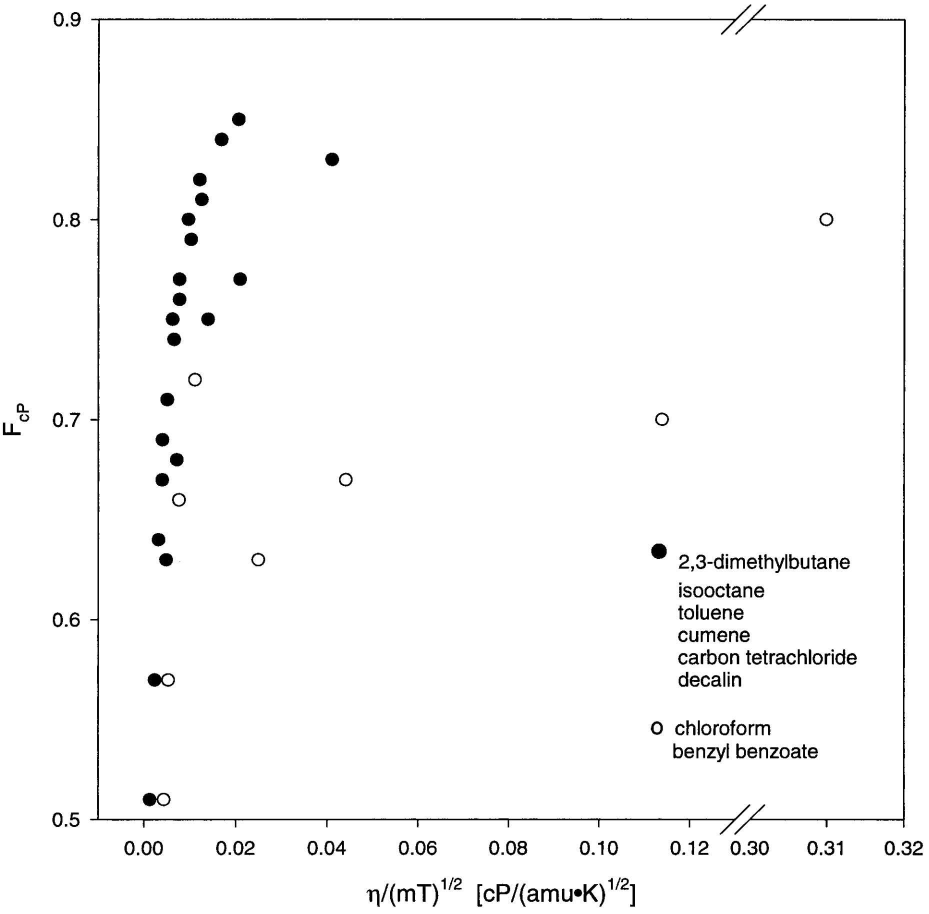
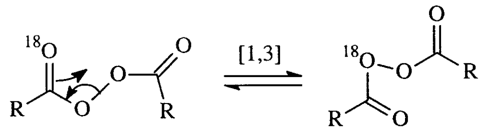


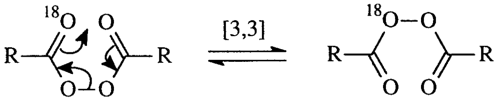
Fig. 5. Cage effect ($F_{cP}$) versus $\eta/(mT)^{1/2}$ for methyl radicals [69] in nonpolar solvents (●) and in polar solvents (○).

## 7. A picture of solvent cage effects

Why is the cage recombination efficiency of polar radicals insensitive to solvent polarity? The findings discussed above are surprising, given that the radicals involved have large dipole moments [59] and should interact strongly with polar solvents such as alcohols. To explain these observations, it is necessary to consider the time scales for molecular rotation and translational diffusion for molecules in liquids. It is also important to note that molecular radicals generally require a certain mutual orientation in order to react with each other, and because geminate radicals are formed from homolysis of a bond in a parent molecule, they are initially aligned for recombination. Therefore any process that changes the mutual orientation of the radicals and prevents realignment will reduce the magnitude of the cage effect. This process would be in addition to diffusion out of the solvent cage and would increase the value of $k_d$ in the expression for $F_c$ above. Polar solvent molecules can reorient polar radicals through electrostatic interactions, and any solvent molecule, polar or nonpolar, could reorient the radicals through collisions. A solvent polarity effect would be expected if the time scale for radical reorientation due to electrostatic interactions with the solvent is appreciably faster than the time scale for collisions. Molecular dynamics simulations indicate that the collision frequency between molecules in liquids is on the order of 100 fs [78,79]. Time-resolved absorption spectroscopy studies on $Mn_2(CO)_{10}$ [80] and on $M(CO)_6$ ($M = Cr$, Mo, W) [81] showed that geminate recombination also takes place in the subpicosecond regime. It seems unlikely that reorientation through electrostatic interactions would be significantly faster than 100 fs.

Some isotope-scrambling and racemization studies seem to suggest that molecular reorientation can occur faster than geminate recombination [7]. However, most of these experiments involved compounds containing molecular spacers in which the geminate radicals were created with a molecule of $N_2$ or $CO_2$ between them. In such cases, the cage products that showed a scrambled label or racemized center must be formed after the spacer molecule has diffused out of the cage. The diffusion of spacer molecules out of the cage is not fast enough to be ignored, and scrambling or racemization of the radical could occur in the intervening time. In those experiments not involving loss of a spacer, a change in mechanism may account for the scrambling. For example, in the case of acetyl peroxide [82–84] and benzoyl peroxide [85] containing $^{18}O$ in one of the carbonyl groups, the cage product does not form after loss of a spacer molecule, yet isotopic scrambling still occurs.





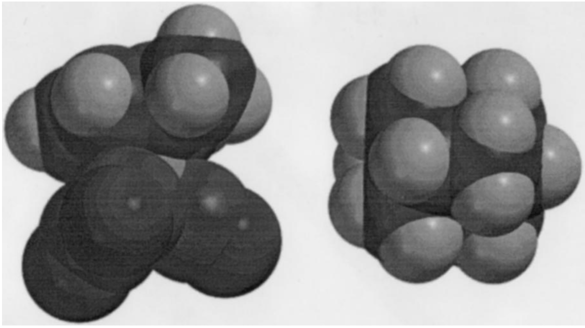


Fig. 6. Space filling models of adamantane (right) and Cp′Mo(CO)$_3$ (left) showing the similarities in their sizes.

However, as pointed out by Goldstein and Judson, acyl peroxides are subject to a 1,3- or 3,3-sigmatropic shift, which can intramolecularly scramble the labeled oxygens [86,87], and these routes may account for the scrambling:

In order to gain more insight into the rates of molecular rotation in the solvents used in our study, we determined the rotational correlation times of adamantane-$d_{16}$ in four of the solvent systems using NMR $T_1$ measurements. Adamantane was chosen because it is similar in size and shape to the Cp′Mo(CO)$_3$ radical (Fig. 6). Furthermore, it is rigid and nonpolar, and it makes an ideal probe of solvent dynamics because its motion is controlled primarily by collisions with the solvent molecules rather than by electrostatic interactions or internal motion. The rotational correlation times for adamantane-$d_{16}$ fell in the range 1.4–2.3 ps over the viscosity range 0.35–27.7 cP. The Cp′Mo(CO)$_3$ radical has a greater mass and therefore a greater moment of inertia, and because it is polar, it should experience more frictional drag through electrostatic interactions with polar solvent molecules. For these reasons, the Cp′Mo(CO)$_3$ radical would be expected to tumble more slowly than adamantane [88].

Because collisions with the solvent molecules are so frequent and tend to randomize molecular orientation, true geminate recombination may only be possible after one or two collisions of the radicals; after that, the molecules are no longer properly aligned, and may diffuse apart before accidental realignment occurs. This model of fast geminate recombination was also proposed by Harris et al. for the photolysis of $CH_2I_2$ [79], and it certainly seems applicable to much larger molecules such as Cp$'_2$Mo$_2$(CO)$_6$. Our explanation for the lack of a solvent polarity effect is that radical reorientation due to electrostatic (i.e. ‘polar’) interactions is not significantly faster than the random reorientation due to collisions with solvent molecules. The fact that there is nevertheless a solvent dependence suggests that the dynamic properties of the solvent are more important than the static properties. In this case, it will be necessary to use ultrafast laser spectroscopy and molecular dynamics simulations to further explore solvent cage effects. These experiments are underway in our laboratory.

## Acknowledgements

The National Science Foundation is acknowledged for support of this work.

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