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Cage Effects in Organometallic Radical Chemistry. Fractional Cage-Recombination Efficiency for Photochemical Caged-Pair Intermediates of $Cp'_2M_2(CO)_6$ (M = Mo and W; Cp' = η^5-$C_5H_4CH_3$)

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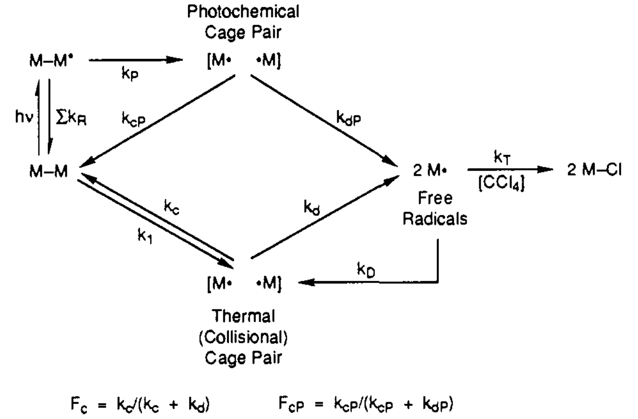
Abstract: A new method is reported for measuring photochemical cage-efficiency factors, F_{cP}, in photochemically generated radical cage pairs. (The photochemical cage-efficiency factor is defined as $k_{cP}/(k_{cP} + k_{dP})$, where k_{cP} is the rate constant for cage recombination of a photochemically generated radical cage pair and k_{dP} is the rate constant for cage escape.) The method was applied to the measurement of F_{cP} values for $[Cp'(CO)_3M^{\bullet\bullet}M(CO)_3Cp']$ caged pairs (M = Mo, W) in solvent systems of various viscosities. The results show that there is a significant cage effect even in common solvents. For example, F_{cP} is predicted to be $\simeq 0.3$ for the $[Cp'(CO)_3Mo^{\bullet}\,^{\bullet}Mo(CO)_3Cp']$ caged pair in cyclohexane at 23 °C.

Cage effects[1-3] have an enormous impact on organic chemical reactivity in solution. They are responsible for magnetic isotope[4] and CIDNP[5] effects, rate–viscosity correlations,[6] variations in quantum yields,[1,7] products, and product yields as a function of medium,[8] and a host of other phenomena. Furthermore, a quantitative knowledge of cage effects is important for the proper interpretation of bond dissociation measurements made in solution,[9] activation parameters,[10] and mechanistic aspects of radical reactions.[11-13] In contrast to the relative wealth of information on cage effects in organic systems, very little is known about cage effects in *organometallic* systems. In fact, with the exception of several papers[11-13] and a 1988 review,[9] the impact of cage effects on organometallic radical reactivity is almost universally ignored.[14] With this situation in mind, we have begun a research program to investigate cage effects in organometallic chemistry.

Scheme I[a]



[a] M = $Cp'Mo(CO)_3$ or $Cp'W(CO)_3$; $\sum k_R$ represents all "non-caged-pair-forming" deactivation pathways.

The information most important in the quantitative study of cage effects is the "cage-efficiency factor", F_c or F_{cP}.[3,9] (The subscript "P" is appended to differentiate photochemical from thermal pathways; see Scheme I for definitions.) In this article, we report a new method for measuring F_{cP} values. The method is applied to the study of radical cage pairs formed by photolysis of the M–M bonds in $Cp'_2M_2(CO)_6$ (M = Mo, W; Cp' = η^5-$C_5H_4CH_3$); however, the method is general and can be applied to virtually any photochemical system. The results indicate that cage effects can be substantial for the $Cp'_2M_2(CO)_6$ molecules even in ordinary solvent systems.

Results and Discussion

Our new method for the determination of F_{cP} values in photochemical systems is experimentally based on the measurement of radical-trapping quantum yields as a function of viscosity. The

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[14] Cage effects in organometallic systems have not been studied with the same rigor as other phenomena because cage effects are usually "hidden" from ordinary kinetic observations. Even in organic systems, the study of cage effects (and the determination of F_{cP} values, in particular) requires substantial effort. For example, F_c values in the reversible thermolysis of peroxy esters[3b] and diacyl peroxides[15] were studied by oxygen-18 randomization rates.

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Table I. Quantum Yields[a] for Reaction with CCl_4 and F_{cP} Values for $Cp'_2Mo_2(CO)_6$ and $Cp'_2Mo_2(CO)_6$ at Various Viscosities and 23 °C

solvent[b] (mL of paraffin oil)	viscosity (cP)	$[Cp'Mo(CO)_3]_2$		$[Cp'W(CO)_3]_2$	
		Φ_{obsd}	F_{cP}	Φ_{obsd}	F_{cP}
0	0.30 ± 0.01	0.51 ± 0.05	0.12 ± 0.02	0.51 ± 0.05	0.28 ± 0.05
10	0.43 ± 0.01	0.44 ± 0.05	0.16 ± 0.02	0.41 ± 0.04	0.35 ± 0.05
30	0.93 ± 0.03	0.40 ± 0.04	0.28 ± 0.03	0.27 ± 0.03	0.52 ± 0.06
40	1.50 ± 0.05	0.34 ± 0.04	0.37 ± 0.04	0.31 ± 0.03	0.62 ± 0.08
50	2.44 ± 0.10	0.28 ± 0.03	0.47 ± 0.06	0.16 ± 0.02	0.70 ± 0.09
60	3.77 ± 0.10	0.20 ± 0.02	0.55 ± 0.08	0.15 ± 0.02	0.76 ± 0.10
70	11.37 ± 0.40	0.10 ± 0.01	0.69 ± 0.11	0.05 ± 0.005	0.85 ± 0.10

[a] 550 nm; $[CCl_4]$ = 2 M. [b] Solvents were prepared by adding the indicated volume of paraffin oil to 19.6 mL of CCl_4 and enough hexane to total 100 mL.

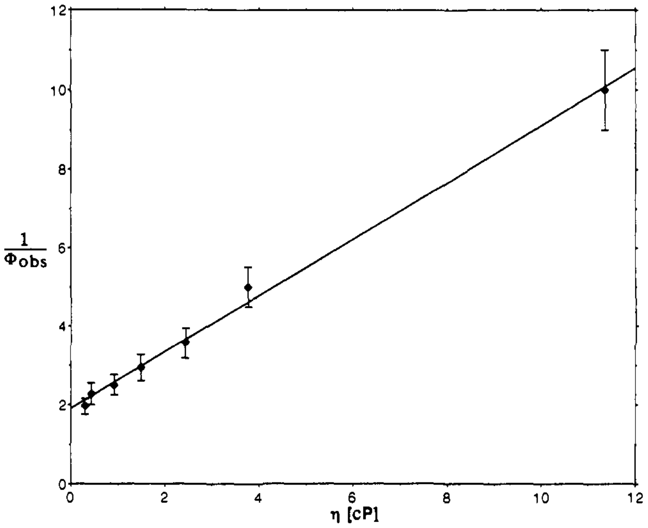

Figure 1. Plot of Φ^{-1} vs viscosity for the photochemical reaction (λ = 550 nm) of $Cp'_2Mo_2(CO)_6$ with CCl_4 (2 M). All error bars represent $\pm 2\sigma$.

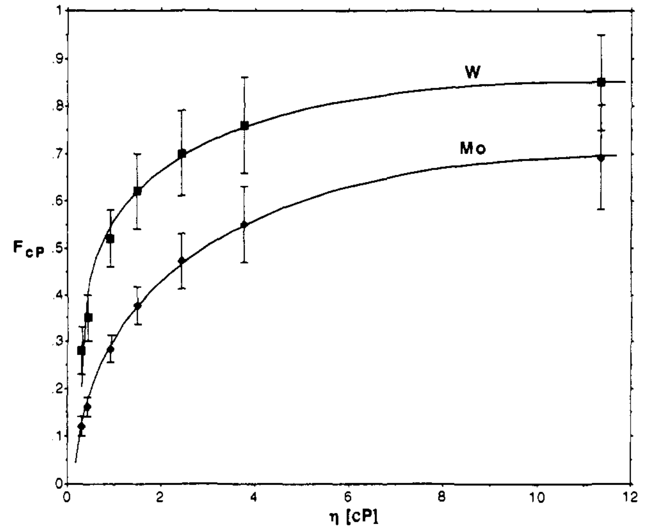

Figure 2. Plots of F_{cP} as a function of viscosity for $Cp'_2M_2(CO)_6$ (M = Mo, W) at 23 °C.

reaction chosen to illustrate the method is the reaction of $Cp'_2Mo_2(CO)_6$ with CCl_4:

$$Cp'_2Mo_2(CO)_6 + 2CCl_4 \xrightarrow{h\nu} 2Cp'Mo(CO)_3Cl\ [+\ 2^{\bullet}CCl_3] \qquad (1)$$

This reaction has been extensively studied,[16] and the pathway is shown in Scheme I.[17] With sufficiently high concentrations of trap, collisional caged pair formation (k_D) can be suppressed so that all radicals which escape the cage will form the Cp'Mo(CO)$_3$Cl product (Scheme I).[21] Under conditions of complete free radical trapping, the reciprocal of the quantum yield for disappearance of the $Cp'_2Mo_2(CO)_6$ complex will be given by eq 2, where Φ_{pair} is the quantum yield for formation of the caged pair

$$1/\Phi_{obsd} = [1/\Phi_{pair}][1 + k_{cP}/k_{dP}] \qquad (2)$$

$[\Phi_{pair} = k_P/(k_P + \sum k_R)]$. Rearrangement of eq 2 yields eq 3, from which it is clear that F_{cP} can be calculated if Φ_{pair} and Φ_{obsd} are known. Because Φ_{obsd} can be measured, the problem of determining F_{cP} thus becomes one of determining Φ_{pair}.

$$\Phi_{obsd}/[\Phi_{pair} - \Phi_{obsd}] = k_{dP}/k_{cP} = [1/F_{cP}] - 1 \qquad (3)$$

Φ_{pair} was determined by measuring the quantum yields for reaction 1 as a function of solvent viscosity. The solvent was a mixture of hexane, paraffin oil, and CCl_4 (2 M), and the viscosity was varied by changing the fraction of paraffin oil in the mixture. (Solvent mixtures with a constant fraction of alkane (see Table I) were chosen in order to keep the solvation of the radicals constant in the various solvent mixtures.[24]) Figure 1 shows that the reciprocals of the observed quantum yields give a linear correlation with solvent viscosity. If Φ_{pair} is assumed to be a constant in the solvent series then the intercept of this plot is equal to the reciprocal of Φ_{pair}. That the intercept is equal to the reciprocal of Φ_{pair} is shown by eq 2: the second term on the right-hand side is expected to contain a viscosity dependence such that k_{cP}/k_{dP} becomes much smaller than 1 as the viscosity approaches zero. Thus, at zero viscosity (infinite fluidity), Φ_{obsd} will equal Φ_{pair}. The value of Φ_{pair} obtained from the intercept is 0.53 ± 0.05 at 23 °C. This value suggests that the "non-pair-forming" return pathways ($\sum k_R$) of Scheme I are comparable to k_P.

Once the value of Φ_{pair} was determined, the cage-efficiency factors (F_{cP}) were calculated by first plotting $\Phi_{obsd}/[\Phi_{pair} - \Phi_{obsd}]$ vs viscosity^{-1} (i.e., $1/F_{cP} - 1$ vs viscosity^{-1}), as indicated in eq 3. (The plot is provided as supplementary material.) Values of F_{cP} at various viscosities were then calculated from the best-fit line in this plot. A plot of F_{cP} as a function of viscosity for the $Cp'_2Mo_2(CO)_6$ complex is shown in Figure 2.

F_{cP} values for $Cp'_2W_2(CO)_6$ were obtained by an analogous route (Figure 2). Note that the F_{cP} values are slightly higher for

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(17) The generation of CCl_3 radicals in this reaction could lead to a radical chain mechanism.[18] However, a comparison of the results using CCl_4 as a trap to those using TMIO as a trap showed there was no chain component to reaction 1.[19] TMIO[20] is a nitroxide radical trap for which no chain reaction is possible.

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(21) The rate constant[22] for chlorine transfer between the $Cp'(CO)_3M^{\bullet}$ free radical and CCl_4 (k_T, Scheme 4) is 2×10^4 M^{-1} s^{-1}. Thus, a 2 M concentration of CCl_4 is more than an order of magnitude greater than that needed for complete trapping of the low (10^{-9} M) steady-state concentration of $Cp'(CO)_3M^{\bullet}$ free radicals formed in our experiments,[23] even in the most viscous of our solvent systems.

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(24) It should be noted that changes in the polarity of the medium will superimpose additional solvent effects over and above the changes due to viscosity. Variations due to F_{cP} could well be masked by specific solvent effects.

$Cp'_2W_2(CO)_6$ than for $Cp'_2Mo_2(CO)_6$. (The value of Φ_{pair} (0.63 + 0.06) was also slightly higher for the W dimer.) Several factors may account for the larger F_{cP} values for the $[Cp(CO)_3W^\bullet\,{}^\bullet W(CO)_3Cp]$ caged pair compared to the analogous Mo cage pair. One possible factor is the smaller difference between the bond dissociation energy and the photochemical excitation energy for $Cp'_2W_2(CO)_6$ compared to $Cp'_2Mo_2(CO)_6$ ($h\nu$ = 52 kcal/mol; $D_{W-W} \approx 56$ kcal/mol;[25] $D_{Mo-Mo} \approx 32$ kcal/mol[26]). For small organic radicals, it is well-established that an increase in the photochemical excitation energy leads to a decrease in F_{cP}, a result attributed to an increase in the translational energy of the photogenerated radicals.[27] A similar effect may be at work here. On the other hand, if the excess excitation energy is rapidly dispersed, the larger F_{cP} value for the W dimer may be a reflection of the increased driving force (and consequently lower activation barrier) for recombination of the two $Cp(CO)_3W^\bullet$ radicals compared to the $Cp(CO)_3Mo^\bullet$ radicals.

Another possible explanation for the difference in F_{cP} values between $Cp'_2W_2(CO)_6$ and $Cp'_2Mo_2(CO)_6$ is the increase in spin–orbit coupling for W compared to Mo. The increase will facilitate intersystem crossing, and this would manifest itself in a larger Φ_{pair} as well as a faster recombination rate constant k_{cP}. (Φ_{pair} will increase because intersystem crossing to the dissociative triplet state will increase and, hence, k_P will be larger relative to $\sum k_R$.) A final factor that may account for the larger F_{cP} values in the W dimer is the difference in mass between the $Cp(CO)_3W^\bullet$ and $Cp(CO)_3Mo^\bullet$ radicals. Noyes[2b,3a] predicted that diffusional rate constants such as k_{dP} would be sensitive to size and mass effects, but no method is currently available for predicting how such factors will affect F_{cP} values for the $Cp'(CO)_3M^\bullet$ radicals. In summary, the higher F_{cP} values for the $[Cp'(CO)_3W^\bullet\,{}^\bullet W(CO)_3Cp']$ caged pair compared to $[Cp'(CO)_3Mo^\bullet\,{}^\bullet Mo(CO)_3Cp']$ may be attributable to a number of factors. Further investigation of these factors provides a rich area for future research.

It should be emphasized that the present analysis rests on the assumption of a constant value for Φ_{pair} over the range of solvent mixtures used in this study. This assumption is not likely to be precisely valid, but no direct experiments have been reported in any system to suggest whether Φ_{pair} is or is not constant. A previous study by Koenig[29] on the thermolysis of peracetates did find a small variation of k_1 (the thermal analogue of Φ_{pair}) with viscosity, but the variation was minor. In the absence of experimental results, the assumption is typically made that k_d (or k_{dP}) is the only viscosity-dependent rate constant.[3a,6b] The viscosity dependence of Φ_{pair} is another area for future research.

The validity of the assumption that Φ_{pair} is constant (or reasonably so) is supported by the agreement between the derived F_{cP} values and the F_{cP} values estimated from the formula $k_t = F_c k_D$, where k_t is the rate constant for self-termination of the organometallic free radicals and k_D is the diffusion-controlled rate constant for a particular solvent. The experimental values for self-termination of organometallic free radicals are near 10^9 M^{-1} s^{-1}, e.g., $k_t = 3.2 \times 10^9$ M^{-1} s^{-1} for $Cp(CO)_3Mo^\bullet$ coupling in acetonitrile ($\eta \simeq 0.35$ cP, 20 °C).[16a] Diffusion-controlled rate constants are calculated approximately using the Smoluchowski equation:[2b] $k_{D,\text{acetonitrile},20\,°C} \simeq 2.7 \times 10^{10}$ M^{-1} s^{-1}. Thus, $F_c \simeq 0.12$ for $[Cp(CO)_3Mo^\bullet\,{}^\bullet Mo(CO)_3Cp]$ in acetonitrile, a value reasonably close to the value of 0.14 in Figure 2 for hexane/CCl_4/paraffin oil at this viscosity (but at 23 °C).

In summary a new method was developed for the determination of F_{cP} values in photochemical systems. The F_c results in Figure 2 demonstrate that the cage effect in the $Cp'_2M_2(CO)_6$ systems can be substantial even in common solvents. For example, if the cage effect in cyclohexane (1.06 cP at 20 °C) is comparable to the cage effect of the mixed hexane/paraffin oil solvent at the same viscosity then an F_c value of about 0.3 is expected. Finally, it is worth emphasizing again that, while the new method was illustrated for the case of an organometallic radical reaction, the method can also be applied to the investigation of organic and inorganic radical systems as well as to nonradical reactions.

Experimental Section

All manipulations were carried out in the absence of water and atmospheric oxygen using standard Schlenk and drybox techniques. $Cp'_2Mo_2(CO)_6$ and $Cp'_2W_2(CO)_6$ were prepared by the method of Birdwhistell,[31] recrystallized twice from THF/hexane, and dried in vacuo prior to use. Solutions of $Cp'_2M_2(CO)_6$ are light-sensitive and were protected from light. *n*-Hexane (HPLC, Aldrich) was distilled from sodium, CCl_4 (Baker) was distilled twice from P_2O_5, and Nujol (Spectrum) was stirred over sodium and then filtered to remove the sodium. All solvents were degassed by repeated freeze–pump–thaw cycles and stored in amber bottles under N_2.

The mixed solvent systems were prepared in a darkened glovebox. All solutions were 2 M in CCl_4, with varying ratios of hexane and Nujol (from 0–87% Nujol; Table I). Kinematic viscosities of the solutions were measured with calibrated Cannon-Fenske viscometers and corrected to absolute viscosity. Solutions of $Cp'_2M_2(CO)_6$ (0.6 M) were prepared in a darkened glovebox and transferred to 1-cm cuvettes equipped with a magnetic stir bar and an attached freeze–pump–thaw bulb. The samples were degassed by four freeze–pump–thaw cycles and then thermally equilibrated for at least 1 h. The quantum yields reported in Table I are the average of several runs.

Photochemical reactions were carried out with an Oriel 200-W high-pressure mercury arc lamp coupled with a monochromator. Light intensity was determined by actinometry with Aberchrome 540 (Φ_{550} = 0.046).[32] The quantum yields at 550 nm ($I_a = 3.6 \times 10^{-9}$ einstein/s) were determined by initial (<10%) rates of $Cp'_2M_2(CO)_6$ disappearance as monitored by the disappearance of the $d\pi \rightarrow \sigma^*$ transition (M = Mo, 506 nm; M = W, 490 nm). There is no measurable dark reaction during the quantum yield measurement (45–60 min). The stirred cells were maintained at 23 ± 1 °C with a flow of compressed air through the cell holder during photolysis to prevent warming and thermal reaction. All quantum yields were corrected with a linear correction for nonabsorption.

Acknowledgment is made to the National Science Foundation for the support of this work.

Supplementary Material Available: Plot of $\Phi_{obsd}/(\Phi_{pair} - \Phi_{obsd})$ vs η^{-1} for $Cp'_2Mo_2(CO)_6$ (1 page). Ordering information is given on any current masthead page.

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[26] (a) Landrum, J. T.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 215–224. (b) Amer, S.; Kramer, G.; Poë, A. J. *J. Organomet. Chem.* **1981**, *209*, C28–C30.

[27] We note that picosecond laser photolysis of $Mn_2(CO)_{10}$ indicated a very low photochemical cage-recombination efficiency in ethanol (viscosity ca. 1 cP).[28] The high photochemical energy deposition and low bond energy for the $Mn_2(CO)_{10}$ study in ref 28 indicate that the F_{cP} value should be much less than the $F_{cP} \simeq 0.3$ value found in the $Cp'_2M_2(CO)_6$ study reported herein.

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[29] Koenig, T.; Huntington, J.; Cruthoff, R. *J. Am. Chem. Soc.* **1970**, *92*, 5413–5418.

[30] See footnote 27 for a cautionary note which points out that the photochemical input energy may be an important factor in determining F_{cP}.

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[32] Heller, G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341–343.