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Cage Effects in the Photochemical Degradation of Polymers. Studies of Model Complexes with Different Chain Lengths

Jonathan L. Male, Britt E. Lindfors,
Katharine J. Covert,† **and David R. Tyler***

Department of Chemistry, University of Oregon,
Eugene, Oregon 97403

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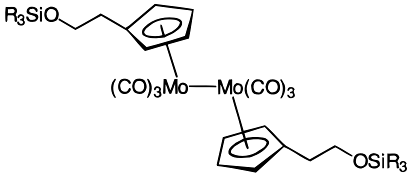
Polymers with metal–metal bonds along their backbones react photochemically with visible light by a mechanism involving metal–metal bond homolysis followed by capture of the metal radicals with either oxygen or other traps (Scheme 1).[1]

In recent papers, we showed that the quantum yields for the degradation of these polymers and model complexes decreased as the chain lengths increased.[1] This is an expected result because the quantum yields for the photodegradation of polymers are generally dependent on the chain length of the molecule. For example, Guillet showed that quantum yields for the Norrish type I or type II degradations of various model aliphatic ketones varied as a function of chain length.[2,3] Reasons for the dependence of the quantum yields on the chain length have been a matter of considerable interest and speculation.[3] It is generally hypothesized[2] that the dependence is attributable either to changes in ϕ_{pair} (the quantum yield for the formation of the radical cage pair; Scheme 2) or to changes in the cage effect as the chain length is varied. (The cage effect, denoted F_{cP}, is defined as the ratio of the rate constant for cage recombination (k_{cP}) to the sum of the rate constants for all cage processes ($k_{\mathrm{cP}} + k_{\mathrm{dP}}$, for the case in Scheme 2), where k_{dP} is the diffusion rate constant.[4–7,9]) In order to gain a greater insight into the role that the chain length plays in the efficiency of polymer photochemistry, we synthesized the series of polymer model molecules $(CpCH_2CH_2OSiR_3)_2Mo_2(CO)_6$ (R = Me, *i*-Pr, *n*-Pr, *n*-Hx) (**1a–d**), and we determined ϕ_{pair} and F_{cP} for each. This communication reports the results of our study and the implications they have for the photochemical cleavage of polymer backbones.[10]



1a–d

1a, R = Me; **1b**, R = *i*-Pr; **1c**, R = *n*-Pr; **1d**, R = *n*-Hx

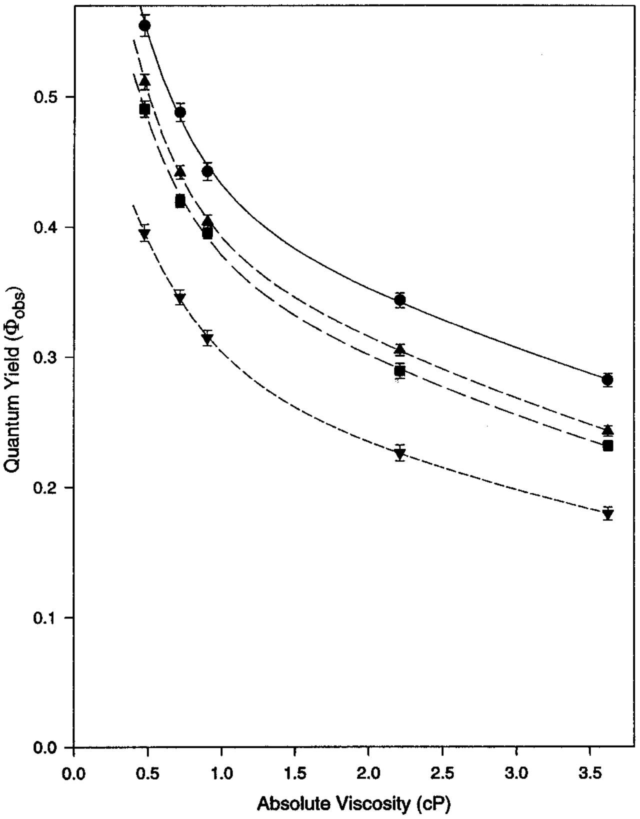
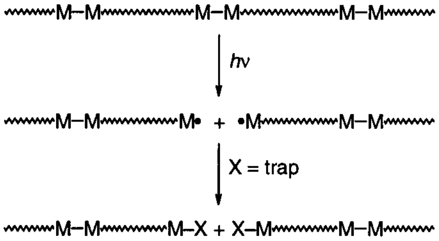
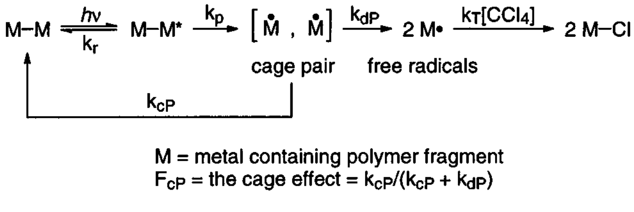


Figure 1. Plot of Φ_{obs} vs viscosity for the photochemical reaction (λ = 540 nm) of $(CpCH_2CH_2OSiR_3)_2Mo_2(CO)_6$ [R = Me (●), *i*-Pr (▲), *n*-Pr (■), *n*-Hx (▼)] with CCl_4 (2 M) at 23 ± 1 °C. All error bars represent $\pm 1\sigma$.

Scheme 1



Scheme 2. Reaction Scheme for Metal–Metal Bond Photolysis



The four derivatized $Cp_2Mo_2(CO)_6$ (**1a–d**) molecules used in this study were synthesized by the route shown in eq 1.[11–13] The molecules were obtained rigorously pure by repeated filtrations and recrystallizations from hexanes.

$$\begin{aligned}&(CpCH_2CH_2OH)_2Mo_2(CO)_6\\ &\xrightarrow[-80\ {}^\circ C,\ THF]{n\text{-BuLi}} \text{"}(CpCH_2CH_2OLi)_2Mo_2(CO)_6\text{"}\\ &\xrightarrow[-80\ {}^\circ C,\ THF]{R_3SiCl} (CpCH_2CH_2OSiR_3)_2Mo_2(CO)_6\end{aligned} \qquad (1)$$

The electronic spectra of the molecules are essentially identical.[14] This point is important because it suggests that changes in the photophysical parameters will only be caused by differences in the lengths of the sidechains

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† Present address: Department of Chemistry, West Virginia University, Morgantown, WV 26506-6045.

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Table 1. Quantum Yields, Molecular Masses, Volumes, and Cage Efficiencies (F_{cP}) for the $(CpCH_2CH_2OSiR_3)_2Mo_2(CO)_6$ (R = Me, *i*-Pr, *n*-Pr, *n*-Hx) Molecules

compd $(CpCH_2CH_2OSiR_3)_2Mo_2(CO)_6$	ϕ_{pair}	Φ_{obs}[a]	F_{cP}[a]	mol mass[b]	static mol vol of (Å^3)[b,c]	approx dynamic mol vol (Å^3)[b,d]
R = Me	0.61 ± 0.02	0.282 ± 0.005	0.54 ± 0.02	361.30	185	695
R = *i*-Pr	0.56 ± 0.02	0.243 ± 0.003	0.57 ± 0.03	445.45	265	994
R = *n*-Pr	0.55 ± 0.02	0.232 ± 0.004	0.58 ± 0.02	445.45	262	1330
R = *n*-Hx	0.46 ± 0.02	0.179 ± 0.005	0.62 ± 0.03	571.71	395	2750

[a] $\lambda = 540$ nm, at viscosity of 3.62 cP and 23 ± 1° C, all error bars represent ± 1σ. [b] Of the mononuclear radical fragment. [c] The static molecular volumes of the dimeric molecules were calculated by using the computer program Steric (written by B. Craig Taverner, Department of Chemistry, University of the Witwatersrand, Private Bag 3, WITS 2050, Johannesburg, South Africa) and then halved to yield the approximate volume of the radical fragment. [d] The approximate dynamic volumes were calculated from the models of the dimers generated in Spartan and measuring the maximum distance across the molecule and dividing this by four and taking this as the radius of the sphere the radical fragment would generate upon rapid isotropic rotation.

and not by electronic differences in the metal−metal bond chromophores.[16]

The cage effects and ϕ_{pair} for **1a**−**d** were measured using a previously reported method in which the quantum yields for the reactions with a radical trap are measured as a function of viscosity.[9,17] The radical trap used in these experiments was CCl_4 (eq 2; Scheme 1).

$$(CpR)_2M_2(CO)_6 \xrightarrow[CCl_4,\ \text{hexane/paraffin oil}]{h\nu\ (540\ \text{nm})} 2(CpR)M(CO)_3Cl \qquad (2)$$

The quantum yields for reaction 2 were measured in hexane solution, and paraffin oil was used to increase the viscosity.[18] There is no back-reaction of the free radicals under the reaction conditions because the concentration of CCl_4 (2 M) is high enough to trap every free radical.[19] Quantum yields for the reactions with CCl_4 as a function of viscosity are shown in Figure 1 for the four $-OSiR_3$ dimers. Note that at any given viscosity the quantum yields generally decrease in the order $-OSiMe_3$ > $-OSi(i\text{-}Pr)_3$ > $-OSi(n\text{-}Pr)_3$ > $-OSi(n\text{-}Hx)_3$; i.e., the quantum yields decrease as the chain length increases, a result that suggests these molecules are good models for the metal−metal bond containing polymers, which showed similar behavior. From the intercept in the plot of Φ^{-1}_{obs} vs viscosity, the values of ϕ_{pair} were obtained (see Table 1 and the Supporting Information). These values were used to calculate the cage effects (F_{cP}),[17] which are shown in Figure 2 as a function of viscosity.

Three trends in Figure 2 and Table 1 are important. First, the cage effect increases with increasing length of the substituent on the Cp ligand [$CH_2CH_2OSiMe_3$ < $CH_2CH_2OSi(i\text{-}Pr)_3$ ≤ $CH_2CH_2OSi(n\text{-}Pr)_3$ < $CH_2CH_2OSi(n\text{-}Hx)_3$]. Second, ϕ_{pair} decreases as the chain length increases. Third, note that the difference in the cage effects for the four compounds increases as the viscosity increases (as required by the Stokes−Einstein equation).[20] The first conclusion to be drawn from these results is that both the decrease in ϕ_{pair} and the increase in the cage effect (F_{cP}) contribute to the smaller quantum yields as the chain lengths increase. However, by using eq 3 and looking at the relative changes in ϕ_{pair} and F_{cP} it can be shown that the differences in ϕ_{pair} are largely responsible for the differences in Φ_{obs} at any particular viscosity.

$$\Phi_{obs} = (1 - F_{cP})\phi_{pair} \qquad (3)$$

Thus, even at the highest viscosities, where the differences in the cage effects between the molecules are most pronounced, only about one-third of the difference in Φ_{obs} between **1a** and **1d** is due to the difference in F_{cP} between the two molecules (Table 1). The bulk of the difference is due to the differences in ϕ_{pair} between the two molecules.

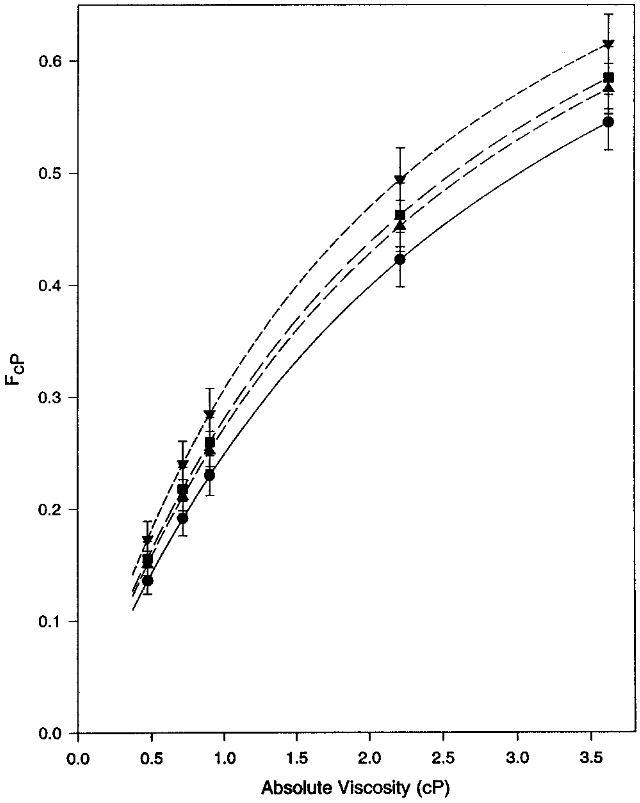

Figure 2. Plot of F_{cP} vs viscosity for $(CpCH_2CH_2OSiR_3)_2Mo_2(CO)_6$ [R = Me (●), *i*-Pr (▲), *n*-Pr (■), *n*-Hx (▼)] with CCl_4 (2 M) at 23 ± 1 °C. All error bars represent ±1σ.

In his mathematical description of the cage effect, Noyes predicted that sterically larger radicals will have greater cage effects, but more massive radicals will have a smaller cage effect.[6] When the chain length is increased, both the size and mass of the radicals are increased (Table 1). The results above are consistent with the effects from increased volume predominating over those of increased mass (if an increase in chain length is taken as representing an increase in size). In fact, as Table 1 shows, the proportional increase in mass is not nearly as large as the proportional increase in size. Note that the competing factors of size and mass might be responsible for the relatively small influence of F_{cP} compared to ϕ_{pair} in their effect on Φ_{obs}. In other words, the change in mass counteracts the influence of the increase in volume on the cage effect as the chain length increases.

The question remains: Why does ϕ_{pair} decrease as the chain length increases? This could be a manifestation of the well-known phenomenon in which radiationless decay is faster in molecules with more vibrational modes.[21]

If the trend of increasing F_c or F_{cP} with chain length continues *ad infinitum* there would be profound consequences for radical chain polymerizations. However, it is likely that a plateau is reached at some chain length, at which point a further increase in chain length will have little effect on F_c or F_{cP}.[2,3] Studies to separate the mass and volume effects on F_c are currently being investigated in our laboratory.

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Supporting Information Available: A table giving Φ_{obs} and F_{cP} for **1a**−**d** at the viscosities shown in Figures 1 and 2 (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1991**, *10*, 1116−1123.

(2) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, England 1985; p 274.

(3) Guillet, J. *Adv. Photochem.* **1988**, *14*, 91−133.

(4) (a) Franck, J.; Rabinowitch, E. *Trans. Faraday Soc.* **1934**, *30*, 120. (b) Rabinowitch, E.; Wood, W. C. *Trans. Faraday Soc.* **1936**, *32*, 138l. (c) Rabinowitch, E. *Trans. Faraday Soc.* **1937**, *33*, 1225. (d) Lorand, J. P. *Prog. Inorg. Chem.* **1972**, *17*, 207−325. (e) Rice, S. A. *Comprehensive Chemical Kinetics;* Elsevier: Amsterdam, The Netherlands, 1985; Vol. 25.

(5) (a) Koenig, T.; Fischer, H. In *Free Radicals*; Kochi, J., Ed.; John Wiley: New York, 1973; Vol. l, Chapter 4. (b) Koenig, T. In *Organic Free Radicals*; Pryor, W. A., Ed.; ACS Symposium Series 69; American Chemical Society: Washington, DC, 1978; Chapter 3.

(6) (a) Noyes, R. M. *J. Chem. Phys.* **1954**, *22*, 1349. (b) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129. (c) Noyes, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2042. (d) Noyes, R. M. *J. Am. Chem. Soc.* **1956**, *78*, 5486.

(7) An interesting point is that the cage effect for a photochemically formed cage pair does not necessarily equal the cage effect for the same caged pair formed by thermolysis or by diffusional collision of two free radicals.[8]

(8) An excellent discussion of this point with examples is found in ref 5a. Note that this point is related to the point discussed by Noyes[6] wherein the cage effect for a photochemically generated cage pair decreases with increasing photonic energy.

(9) Covert, K. J.; Askew, E. F.; Grunkemeier, J.; Koenig, T.; Tyler, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 10446−10448.

(10) In the past, radical cage pairs were typically generated by the extrusion of small spacer molecules. However, note in our systems that no small spacer molecules are extruded. As pointed out by Lorand[4d] and Koenig,[5a] this leads to a more ideal system for studies of the cage effect.

(11) The derivatized dimers were synthesized under nitrogen as follows: To a −80 °C (dry ice/acetone) solution of $(CpCH_2CH_2OH)_2Mo_2(CO)_6$ in THF was added 2.2 equiv of *n*-BuLi dropwise over 20 min. After 1 h of reaction time, a brick-red solid was allowed to settle. The supernatant was removed via cannula, and the solid was washed twice with THF (20 mL). THF (25 mL) was again added and the mixture was cooled to −80 °C. To the mixture was added 2 equiv of R_3SiCl. The reaction was allowed to proceed until the solution became clear and deep burgundy. After removal of THF *in vacuo*, hexanes were added, and the resulting cloudy burgundy solution was filtered through a fine frit. The products were eluted with hexanes through a short, basic alumina column prior to crystallization from hexanes.

(12) Lindfors, B. E.; Male, J. L.; Covert, K. J.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.*, in press.

(13) Lindfors, B. E.; Male, J. L.; Covert, K. J.; Tyler, D. R. manuscript in preparation.

(14) Each molecule has an intense band at 393 nm ($\epsilon \approx 20\,000$ cm^{-1} M^{-1}), assigned to the $\sigma \rightarrow \sigma^*$ transition, and a weaker band at ≈512 nm ($\epsilon \approx 2000$ cm^{-1} M^{-1}), assigned to a $d\pi \rightarrow \sigma^*$ transition. See ref 15 for further discussion of the electronic structures of these metal−metal bonded molecules.

(15) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187−218.

(16) The $-CH_2CH_2-$ spacer can be thought of as an electronic insulator that reduces any electronic variations on substitution of the alkyl groups. For a similar use of this strategy see Hughes, R. P.; Trujillo, H. A. *Organometallics* **1996**, *15*, 286−294.

(17) Plots of $1/\Phi_{obs}$ vs viscosity are linear with a *y*-intercept equal to $1/\Phi_{pair}$. This value of ϕ_{pair} is then used in the following equation, and the value of F_{cP} is calculated.

$$1/\Phi_{obs} = [1/\phi_{pair}][1 + k_{cP}/k_{dP}]$$

Complete details are found in ref. 9 and 13.

(18) Paraffin oil was used to increase the viscosity because it is a straight-chain hydrocarbon. Thus, we sought to avoid selective solvation, a condition that could complicate the interpretations of the cage effect.

(19) Experiments showed that, as expected, the quantum yields increased with increasing concentration of CCl_4 up to about 0.1 M, at which point saturation in CCl_4 was achieved.

(20) The Stokes-Einstein equation is $D = kT/6\eta\pi r$, where D is the diffusion coefficient of the radical, η is the viscosity, and r is the hydrodynamic radius of the spherical radical. As the viscosity increases, all other terms are constant for a particular molecule, and the diffusion coefficient, which relates to k_d or k_{dP}, will lead to a divergence of the F_c or F_{cP} values for the series of molecules at higher viscosities.

(21) Ferraudi, G. J. *Elements of Inorganic Photochemistry*; Wiley-Interscience: New York, 1988; p 101.

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