

Radical cage effects: A method for measuring recombination efficiencies of secondary geminate radical cage pairs using pump–probe transient absorption methods

Alan B. Oelkers and David R. Tyler*

Received 14th March 2008, Accepted 16th September 2008

First published as an Advance Article on the web 7th October 2008

DOI: 10.1039/b804399j

A method is reported for measuring the recombination efficiency of secondary geminate radical cage pairs. The procedure involves measuring the recombination efficiency for primary geminate recombination (F_{cl}) using pump–probe laser methods and measuring the “apparent” (or net) recombination efficiency (F_{cp}) for all geminate pairs (primary and secondary) using steady-state irradiation methods. A mathematical relationship between F_{cp} , F_{cl} , and F_{c2} (where F_{c2} is the recombination efficiency for secondary geminate recombination) is derived and demonstrated using the photolysis reactions of the $[(CpR)Mo(CO)_3]_2$ molecules, where $CpR = \eta^5-C_5H_4CH_3$ and $\eta^5-C_5H_4(CH_2)_2C(O)NCH_3(CH_2)_nCH_3$ ($n = 3, 8, 13, 18$). As an example of the results obtained using the new method, it was found that $F_{cl} = 0.43$ and $F_{c2} = 0.68$ for the molecule with $CpR = \eta^5-C_5H_4CH_2CH_2N(CH_3)C(O)(CH_2)_{18}CH_3$. The value of F_{c2} decreased as the side-chain on the Cp ring got shorter; F_{c2} is equal to 0.0 for the molecules with $n = 3$ and for $CpR = \eta^5-C_5H_4CH_3$. It is hypothesized that a longer side-chain prevents facile diffusion of the radicals out of the secondary cage, whereas the smaller side-chains permit more facile diffusion apart of the radicals. A general conclusion is that the reactions of large radicals in particular may be especially impacted by secondary geminate cage recombination.

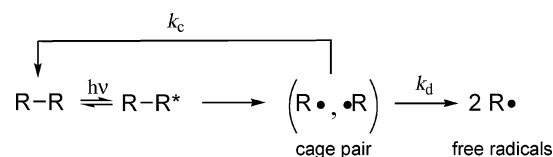
Introduction

The solvent cage effect is vital to understanding the reactivity of radicals generated by bond homolysis reactions in solution.^{1-3†} The term “cage effect” refers to the phenomenon that the probability of recombination of a radical pair is greater in solution than in the gas phase. The origin of this effect is the solvent “cage,” a term introduced by Franck and Rabinowitch in 1934 for a hole in the solvent that temporarily traps a pair of reactive molecules causing them to remain as colliding neighbors for a short period of time before random motion allows their separation.³⁴ The

*Contribution from the Department of Chemistry, University of Oregon,
Eugene, Oregon, 97403, USA. E-mail: dtyler@uoregon.edu; Fax: 1 (541)
346-0487; Tel: 1(541)346-4649*

† Examples of important reactions where cage effects are necessary to explain the reactivity include radical polymerization reactions,^{4,5} the reactions of photosynthetic model complexes, numerous electron transfer reactions,^{6,7} the reactions of coenzyme B₁₂ and its model complexes,⁸⁻¹⁰ and the reactions of hemes with O₂.¹¹ The literature is full of new observations of the cage effect and its impact on reactivity. For example, current areas of intense study include: the repercussions of cage effects in confined media such as micelles, zeolites, and proteins;¹²⁻¹⁴ the role of the cage effect in describing the kinetics of high energy materials;¹⁵ the impact of the cage on the stereospecificity of reactions;¹⁶ biochemical toxicity;¹⁷ super-critical fluids;¹⁸ polymer degradation reactions;¹⁹ luminescence and quenching;²⁰ bond cleavage energetics;²¹ and metal complex photochemistry.²² Furthermore, cage effects are necessary to explain some of the most fundamental phenomena in physical- and physical-organic chemistry, including magnetic isotope²³ and CIDNP²⁴ effects, rate-viscosity correlations,²⁵ variations in products and yields as a function of medium,²⁶ variations in quantum yields as a function of medium,²⁷ and stereochemical control.²⁸ In addition, analogues of solvent-phase cage effects have now been observed in reactions taking place on surfaces,^{29,30} in gas-phase clusters,^{31,32} and in polymers.^{16,33}

photolysis of a generic molecule in solution to yield a cage pair is shown in Scheme 1.

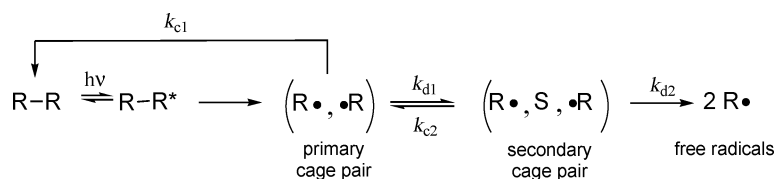


Scheme 1 The photolysis of a generic dimer in solution to yield a radical cage pair. The radicals in the solvent cage can either diffuse apart to yield free radicals or recombine to reform the parent dimer. The rate constants k_c and k_d are for radical–radical recombination and for radical diffusion out of the cage, respectively. No backreaction of the free radicals to the cage pair is shown because, for the steady-state irradiations in this paper, every free radical is captured with a radical trap.

Cage effects are quantitatively assessed by the cage recombination efficiency (F_{cP}),[‡] which is the fraction of geminate radical cage pairs that ultimately recombine.^{3,21} In terms of rate constants, F_{cP} is defined as the ratio of the rate constant for cage recombination to the sum of the rate constants for all competing cage processes. In Scheme 1, $F_{\text{cP}} = k_{\text{c}}/(k_{\text{c}} + k_{\text{d}})$, where the rate constants k_{c} and k_{d} represent the rates of recombination and diffusion, respectively.

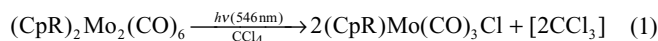
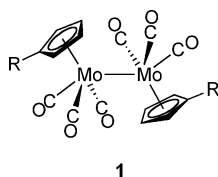
In a series of recent papers, we demonstrated a method for measuring F_{cp} in photochemical reactions using molecules of the

[‡] The rate constants and recombination efficiencies for photochemically and thermally generated cage pairs (that are otherwise identical) are not necessarily the same. To distinguish between the two, the subscript P is often appended to the rate constants and to F_c to indicate that the caged radical pair was generated in a photochemical reaction.



Scheme 2 The photolysis of a generic dimer in solution to yield a primary cage pair and a secondary cage pair. In some solvents, primary geminate radicals that fail to recombine from *secondary geminate pairs* (a solvent-separated cage pair), still retain a reasonable probability of recombination. S in this scheme represents a solvent molecule(s). No backreaction of the free radicals to the secondary cage pair is shown because, for the steady-state irradiations in this paper, every free radical is captured with a radical trap.

type $(\text{CpR})_2\text{Mo}_2(\text{CO})_6$ (**1**; $\text{CpR} = \eta^5\text{-C}_5\text{H}_4\text{R}$; R = a variety of alkyl, silane, and amide chains).^{3,35–37} Using a variety of systematically varying R groups, we investigated how F_{cp} varies as a function of radical mass and size. The method for measuring F_{cp} involves measuring the quantum yield of the photochemical reaction as a function of solvent viscosity.³ The procedure is as follows. For the reaction in eqn (1), which follows the pathway in Scheme 1 with subsequent complete radical trapping by CCl_4 , the quantum yield of $(\text{CpR})_2\text{Mo}_2(\text{CO})_6$ disappearance (Φ_{obs}) is given by eqn (2), where ϕ_{pair} is the quantum yield for formation of the geminate radical cage pair.



$$\Phi_{\text{obs}} = \phi_{\text{pair}}(1 - F_{\text{cp}}) \quad (2)$$

The value of Φ_{obs} is measured experimentally so the problem of obtaining F_{cp} becomes one of finding ϕ_{pair} . To obtain ϕ_{pair} we measure Φ_{obs} as a function of viscosity. As predicted by the Smoluchowski relationship, a plot of Φ_{obs}^{-1} vs. viscosity is linear.³ Extrapolation of this plot to zero viscosity (infinite fluidity) gives ϕ_{pair}^{-1} at the y-intercept. The ϕ_{pair} value thus obtained is then used in eqn (2) to obtain F_{cp} at the various viscosities.[§]

The reaction pathway in Scheme 1 is simplified in that it ignores the possibility of secondary geminate cage pairs and secondary geminate recombination (Scheme 2). Secondary cage effects are those in which the geminate radicals recombine to reform the parent molecule after primary cage escape has occurred but before a random distribution of the radicals in solution is achieved.^{41,42} This paper describes a method to obtain the primary and

Table 1 Cage recombination efficiencies (F_{cl} , F_{c2} , and F_{cp}) at 23 °C for the $(\text{CpR})_2\text{Mo}_2(\text{CO})_6$ molecules, where $\text{R} = \text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{C}(\text{O})(\text{CH}_2)_n\text{CH}_3$ ($n = 18, 13, 8, 3$) and $\text{R} = \text{CH}_3$. The pump–probe experiments to determine F_{cl} were done in cyclohexane (0.89 cP) for $\text{R} = \text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{C}(\text{O})(\text{CH}_2)_n\text{CH}_3$; the F_{cp} values reported for these molecules are for a mixture of hexane and squalane (the latter is a viscosity enhancer) with $\eta = 0.89$ cP. For the molecule with $\text{R} = \text{CH}_3$, the pump–probe experiments to determine F_{cl} and the steady-state experiments to determine F_{cp} were carried out in benzene/squalane with $\eta = 0.73$ cP

Cp ligand	F_{cl}	F_{cp}	F_{c2}
$n = 18$	0.43 ± 0.02	0.70 ± 0.04	0.68
$n = 13$	0.44 ± 0.01	0.59 ± 0.04	0.45
$n = 8$	0.42 ± 0.03	0.48 ± 0.03	0.22
$n = 3$	0.42 ± 0.02	0.42 ± 0.03	0.0
$\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{CH}_3$	0.31 ± 0.01	0.31 ± 0.03	0.0

secondary cage recombination efficiencies using a combination of quantum yield measurements and pump–probe laser experiments.

Experimental

Materials

Hexanes were obtained from Fischer and purified by distillation from potassium benzophenone ketyl under N_2 . Squalane and cyclohexane were obtained from Aldrich and dried using activated 3 Å molecular sieves and deoxygenated by purging with N_2 prior to photolysis studies. $\text{Cp}'_2\text{Mo}_2(\text{CO})_6$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{CH}_3$) was synthesized by a literature method.⁴³ The syntheses of $[(\text{CpR})\text{Mo}(\text{CO})_3]_2$, where $\text{R} = (\text{CH}_2)_n\text{NCH}_3\text{C}(\text{O})(\text{CH}_2)_n\text{CH}_3$ ($n = 3, 8, 13$, and 18) were reported earlier.³⁵ Following synthesis, the purity of the dimers was confirmed using ^1H NMR, IR, UV-vis, LC-MS, and elemental analysis. The samples were dried *in vacuo* before use. The compounds were handled under an N_2 atmosphere in a dark glove-box or on a Schlenk line using standard anaerobic techniques. Solutions were prepared for photolysis studies by dissolving purified samples in neat cyclohexane. The concentrations of the solutions were all approximately 1 mM, chosen to produce a solution with an optical density of approximately 0.5 at 400 nm in the experimental flow cell (pathlength = 0.5 mm). For the pump–probe experiments, the highly air-sensitive cyclohexane/molybdenum dimer solutions were transferred into a vacuum-tight stainless steel reservoir flow cell system, which was deoxygenated with N_2 prior to photolysis studies and maintained under an atmosphere of N_2 during the measurements. The integrity of the solutions was confirmed after completing the photolysis studies by collecting the UV-vis spectra of the solutions.

[§]An alternative method for obtaining ϕ_{pair} is to make the standard assumption³⁸ that the rate constant for geminate recombination, k_{c} , is independent of solvent viscosity (η), and therefore the only viscosity dependence arises from the k_{d} process. (In fact, recent experimental observations confirm that k_{c} is independent of solvent viscosity. See Table 1 in ref. 39) According to the Stokes/Einstein/Smoluchowski equation, $k_{\text{d}} \propto 1/\eta$. Eqn (2) thus becomes $\Phi_{\text{obs}} = \phi_{\text{pair}}/[1 + (\eta/c)]$, where c is a fitting parameter that contains k_{c} . The Φ_{obs} data as a function of viscosity are fit to this equation, which yields a value for ϕ_{pair} . Complete details on this method have been reported.⁴⁰ Note that the values of ϕ_{pair} obtained by this method and by the method reported in the main body of the text are essentially identical.

Methods

The steady-state photochemical technique for the measurement of F_c for geminate radical pairs formed by photolysis of molybdenum dimers has been described in full detail in earlier publications.^{3,35,40,44,45} The femtosecond laser system and the method used to collect pump–probe transient absorption kinetic data were also described earlier.^{18,22}

Results and discussion

Assuming steady-state conditions, the quantum yield (Φ_{obs}) for the disappearance of the starting material (R–R) in Scheme 2 is given by the expression in eqn (3), where ϕ_{pair} is the quantum yield for formation of the primary cage pair; F_{c1} is the cage recombination efficiency for the primary geminate cage ($F_{c1} = k_{c1}/(k_{c1} + k_{d1})$); and F_{c2} is the cage recombination efficiency for the secondary geminate recombination step ($F_{c2} = k_{c2}/(k_{c2} + k_{d2})$).

$$\Phi_{\text{obs}} = \frac{(1 - F_{c1})(1 - F_{c2})\phi_{\text{pair}}}{1 - F_{c2}(1 - F_{c1})} \quad (3)$$

From Φ_{obs} vs. viscosity data, the value of ϕ_{pair} can be obtained as described in the Introduction, which can then be used in eqn (3) to obtain a value for the quantity $[(1 - F_{c1})(1 - F_{c2})/(1 - F_{c2}(1 - F_{c1}))]$ at a particular viscosity. If F_{c1} is known then F_{c2} can be calculated.

Typical time constants for the lifetime of a primary geminate radical pair are on the order of 5 ps or less,^{39,46} and femtosecond timescale laser systems allow one to observe directly the primary recombination event (the k_{c1} reaction) and to obtain F_{c1} . A femtosecond pump–probe study of the $(\text{CpR})_2\text{Mo}_2(\text{CO})_6$ molecule ($\text{CpR} = \eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{C}(\text{O})(\text{CH}_2)_{18}\text{CH}_3$) found a value of 0.43 ± 0.02 for F_{c1} in cyclohexane solvent at 23 °C (0.89 cP).⁴⁶ From steady-state photochemical experiments, a plot of $(\Phi_{\text{obs}})^{-1}$ vs. viscosity gave $\phi_{\text{pair}} = 0.78$.³⁵ Using these values for F_{c1} and ϕ_{pair} and the experimental value of 0.23 for Φ_{obs} in eqn (3) gives a value for F_{c2} of 0.68 under these experimental conditions of temperature and viscosity. To our knowledge, this is the first time a secondary cage recombination efficiency has been reported for a large, multinuclear radical. The results for the $(\text{CpR})_2\text{Mo}_2(\text{CO})_6$ ($\text{CpR} = \eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{C}(\text{O})(\text{CH}_2)_{18}\text{CH}_3$) system are summarized in Scheme 3.

Note that the F_{cP} term in eqn (2), obtained from steady-state measurements, is neither F_{c1} nor F_{c2} but rather an “apparent” (or net) recombination efficiency for all geminate pairs (primary and

secondary). Algebraic manipulation of eqns (2) and (3) yields the expression for F_{cP} in terms of F_{c1} and F_{c2} (eq 4).

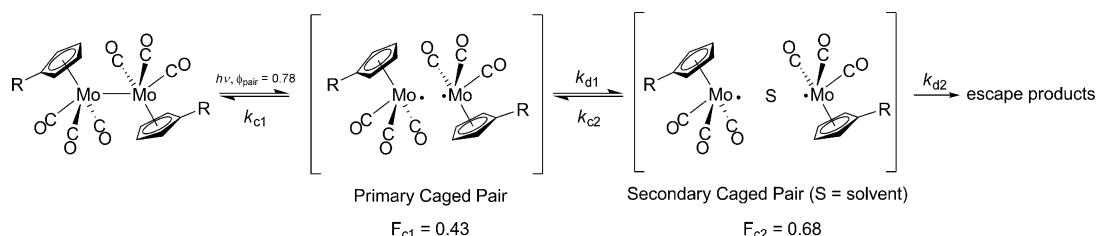
$$F_{cP} = \frac{F_{c1}}{1 - F_{c2}(1 - F_{c1})} \quad (4)$$

This equation provides an alternative (but mathematically equivalent) method to obtain F_{c2} by using F_{cP} obtained from steady-state irradiation experiments and F_{c1} obtained from pump–probe experiments. Using eqn (4), F_{c2} values were obtained for the $(\text{CpR})_2\text{Mo}_2(\text{CO})_6$ molecules, where $\text{R} = \text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{C}(\text{O})\text{-(CH}_2)_n\text{CH}_3$ ($n = 18, 13, 8$, and 3). The data and results are summarized in Table 1. Note there is a decrease in the value of F_{c2} as the length of the side-chain on the Cp ligand shortens in length from $n = 18$ to $n = 3$. In fact, the value of F_{c2} is zero for the $n = 3$ molecule. One conclusion is that secondary geminate recombination is not a significant occurrence in every reaction involving bond cleavage. Further support for this conclusion comes from the photolysis of the $\text{Cp}'_2\text{Mo}_2(\text{CO})_6$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{CH}_3$) molecule in which the side-chain consists of a single methyl group. Laser pump–probe experiments established that $F_{c1} = 0.31 \pm 0.01$ in benzene/squalane ($\eta = 0.73$ cP; 23 °C), and steady-state irradiation experiments found $F_{cP} = 0.31 \pm 0.03$ under the same reaction conditions.³⁶ Substituting these values in eqn (4) yields the result that F_{c2} is zero for this molecule. Because a secondary cage effect is only observed in radicals with long side-chains, it is suggested that the increased length of the side-chain on the Cp ligand prevents facile diffusion of the radicals out of the secondary cage, with a corresponding increase in secondary geminate recombination compared to ligands with shorter side-chains.

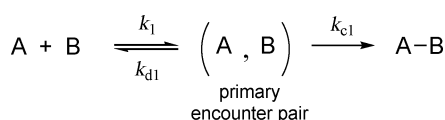
Extension of the results

(1) The equations for the photochemical reactions discussed above are easily converted to the analogous equations for thermal homolysis reactions by replacing ϕ_{pair} with $k_1[\text{R-R}]$, where k_1 is the rate constant for thermolysis of the R–R bond.

(2) Bimolecular thermal reactions also proceed through cage pairs (“encounter complexes”). The reaction involving a single cage pair is shown generically in Scheme 4 and a reaction involving a secondary cage pair is shown in Scheme 5. The relevant rate expressions for bimolecular thermal reactions are also shown in the schemes. (Note that to be consistent with the definitions of F_c in the preceding paragraphs, the F_c values for the reactions in Schemes 4 and 5 are defined in the “forward” direction, e.g., $F_c = k_c/(k_c + k_d)$.) Extension of these rate equations to systems with

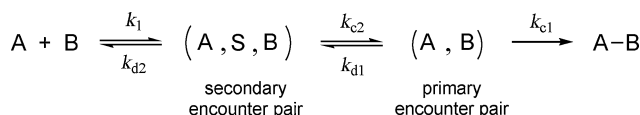


Scheme 3 Primary and secondary cage effect results for the $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{C}(\text{O})(\text{CH}_2)_{18}\text{CH}_3)_2\text{Mo}_2(\text{CO})_6$ molecule in hydrocarbon solvents at 23 °C ($\eta = 0.89$ cP).



$$\text{rate} = F_{c1} \cdot k_1[A][B]$$

Scheme 4 A thermal reaction with a single cage pair.



$$\text{rate} = \left(\frac{F_{c1} \cdot F_{c2}}{1 - F_{c2}(1 - F_{c1})} \right) \cdot k_1[A][B]$$

Scheme 5 A thermal reaction with both a primary and secondary cage pair.

even higher order cage pairs follows a similar pattern that can be written by inspection.

In summary, the results above demonstrate that secondary geminate recombination can be large enough to impact the dynamics of a homolysis reaction. Secondary cage effects are not to be expected in all such reactions, but the results reported herein suggest that the reactions of large radicals in particular may be especially impacted by secondary geminate cage recombination because their diffusion apart is less facile than diffusion in smaller radicals.

Acknowledgements

We thank the NSF for funding through NSF-CHE-0452004 and an NSF IGERT fellowship to A.B.O.

References

- 1 J. P. Lorand, The Cage Effect, *Prog. Inorg. Chem.*, 1972, **17**, 207–325.
- 2 S. A. Rice, *Comprehensive Chemical Kinetics*, Elsevier, Amsterdam, 1985.
- 3 J. L. Male, B. E. Lindfors, K. J. Covert and D. R. Tyler, The Effect of Radical Size and Mass on the Cage Recombination Efficiency of Photochemically Generated Radical Cage Pairs, *J. Am. Chem. Soc.*, 1998, **120**, 13176–13186.
- 4 P. Bosch, J. L. Mateo and J. Serrano, 1-Heptene, 3-heptenes and cumene as model compounds of SBS block copolymers. Study of their photoreactions in the presence of photoinitiators of polymerization, *J. Photochem. Photobiol., A*, 1997, **103**, 177–184.
- 5 J. B. L. De Kock, A. M. Van Herk and A. L. German, Bimolecular free-radical termination at low conversion, *J. Macromol. Sci., Part C: Polym. Rev.*, 2001, **C41**, 199–252.
- 6 H. Knoll, W. J. G. De Lange, H. Hennig, D. J. Stufkens and A. Oskam, Photochemical and thermal disproportionation of $[(CO)_4CoM(CO)_3(LL)]$ ($M = Mn, Re$; $LL = 2,2'$ -bipyridine, 2-pyridinecarboxaldehyde N-isopropylimine) complexes, *J. Organomet. Chem.*, 1992, **430**, 123–132.
- 7 H. K. Van Dijk, J. Van der Haar, D. J. Stufkens and A. Oskam, Metal to ligand charge-transfer photochemistry of metal-metal-bonded complexes. 7. Photochemistry of $(CO)_4CoM(CO)_3(bpy)$ ($M = Mn, Re$; $bpy = 2,2'$ -bipyridine): photocatalytic disproportionation of the manganese complex in the presence of PR3, *Inorg. Chem.*, 1989, **28**, 75–81.
- 8 W. B. Lott, A. M. Chagovetz and C. B. Grissom, Alkyl Radical Geometry Controls Geminate Cage Recombination in Alkylcobalamins, *J. Am. Chem. Soc.*, 1995, **117**, 12194–12201.
- 9 A. G. Cole, L. M. Yoder, J. J. Shiang, N. A. Anderson, L. A. Walker, II, M. M. Banaszak Holl and R. J. Sension, Time-Resolved Spectroscopic Studies of B_{12} Coenzymes: A Comparison of the Primary Photolysis Mechanism in Methyl-, Ethyl-, n-Propyl-, and 5'-Deoxyadenosylcobalamin, *J. Am. Chem. Soc.*, 2002, **124**, 434–441.
- 10 L. M. Yoder, A. G. Cole, L. A. Walker, II and R. J. Sension, Time-resolved spectroscopic studies of B_{12} coenzymes: Influence of solvent on the photolysis of adenosylcobalamin, *J. Phys. Chem. B*, 2001, **105**, 12180–12188.
- 11 T. G. Grogan, N. Bag, T. G. Traylor and D. Magde, Picosecond Reaction of Picket Fence Heme with O_2 and CO: Geminate Recombination in the Solvent Cage, *J. Phys. Chem.*, 1994, **98**, 13791–13796.
- 12 E. E. Scott, Q. H. Gibson and J. S. Olson, Mapping the pathways for O_2 entry into and exit from myoglobin, *J. Biol. Chem.*, 2001, **276**, 5177–5188.
- 13 N. J. Turro, X. -G. Lei, W. Li, Z. Liu, A. McDermott, M. F. Ottaviani and L. Abrams, Photochemical and Magnetic Resonance Investigations of the Supramolecular Structure and Dynamics of Molecules and Reactive Radicals on the External and Internal Surface of MFI Zeolites, *J. Am. Chem. Soc.*, 2000, **122**, 11649–11659.
- 14 J. Sivaguru, A. Natarajan, L. S. Kaanumalle, J. Shailaja, S. Uppili, A. Joy and V. Ramamurthy, Asymmetric Photoreactions within Zeolites: Role of Confinement and Alkali Metal Ions, *Acc. Chem. Res.*, 2003, **36**, 509–521.
- 15 C. F. Melius and M. C. Piqueras, Initial reaction steps in the condensed-phase decomposition of propellants, *Proc. Combust. Inst.*, 2002, **29**, 2863–2871.
- 16 J. Xu and R. G. Weiss, Reaction cavities of liquid and solid phases of a long *n*-alkane, *n*-nonadecane, as probed by the regio- and stereochemical fates of two singlet radical pairs, *Photochem. Photobiol. Sci.*, 2005, **4**, 210–215.
- 17 S. Goldstein and G. Czapski, Viscosity Effects on the Reaction of Peroxynitrite with CO_2 : Evidence for Radical Formation in a Solvent Cage, *J. Am. Chem. Soc.*, 1999, **121**, 2444–2447.
- 18 J. M. Tanko, N. K. Suleman and B. Fletcher, Viscosity-Dependent Behavior of Geminate Caged-Pairs in Supercritical Fluid Solvent, *J. Am. Chem. Soc.*, 1996, **118**, 11958–11959.
- 19 J. Guillet, Photochemistry and molecular motion in solid amorphous polymers, *Adv. Photochem.*, 1988, **14**, 91–133.
- 20 M. Okamoto and F. Tanaka, Solvent and Pressure Effects on Quenching by Oxygen of 9,10-Dimethylanthracene Fluorescence in Liquid *n*-Alkanes: A Study on Solvent Cage Effects, *J. Phys. Chem. A*, 2006, **110**, 10601–10606.
- 21 T. Koenig and R. G. Finke, The cage effect and apparent activation parameters for bond homolysis, *J. Am. Chem. Soc.*, 1988, **110**, 2657–2658.
- 22 J. Farias de Lima, A. K. Nakano and N. Y. M. Iha, Solvent cage effects on the ligand field photochemistry of the cyanoferrate(II) complexes, *Inorg. Chem.*, 1999, **38**, 403–405.
- 23 N. J. Turro and B. Kraeutler, Magnetic field and magnetic isotope effects in organic photochemical reactions. A novel probe of reaction mechanisms and a method for enrichment of magnetic isotopes, *Acc. Chem. Res.*, 1980, **13**, 369–377.
- 24 R. Kaptein, Chemically induced dynamic nuclear polarization: theory and applications in mechanistic chemistry, *Advances in Free-Radical Chemistry (London)*, 1975, **5**, 319–380.
- 25 A. Rembaum and M. Szwarc, O–O bond dissociation energies in propionyl and butyryl peroxides, *J. Chem. Phys.*, 1955, **23**, 909–913.
- 26 D. D. Tanner, H. Oumar-Mahamat, C. P. Meintzer, E. C. Tsai, T. T. Lu and D. Yang, Viscosity-dependent cage reactions. Multiple substitutions in radical-chain chlorinations, *J. Am. Chem. Soc.*, 1991, **113**, 5397–5402.
- 27 R. M. Noyes, Tests of solution models by quantum yields for dissociation, *Z. Elektrochem. Angew. Phys. Chem.*, 1960, **64**, 153–156.
- 28 K. Tomooka, H. Yamamoto and T. Nakai, Stereoselective synthesis of highly functionalized C-glycosides based on acetal [1,2] and [1,4] Wittig rearrangements, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 4500–4502.
- 29 C. J. Jenks, A. Paul, L. A. Smoliar and B. E. Bent, Effects of surface defects and coadsorbed iodine on the chemistry of alkyl groups on copper surfaces: evidence for a cage effect, *J. Phys. Chem.*, 1994, **98**, 572–578.
- 30 A. C. Buchanan, III, P. F. Britt and K. B. Thomas, Radical Chemistry under Diffusional Constraints: Impact of Spacer Molecules on the Thermolysis of Surface-Immobilized Bibenzyl, *Energy Fuels*, 1998, **12**, 649–659.

- 31 A. Kanaev, L. Miseur, F. Edery, T. Laarmann and T. Moller, Cage effect for the photodissociation of H₂O molecules in argon clusters embedded inside neon clusters, *J. Chem. Phys.*, 2002, **117**, 9423–9429.
- 32 V. Vorsa, S. Nandi, P. J. Campagnola, M. Larsson and W. C. Lineberger, Recombination dynamics of photodissociated I₂[−] in size selected Ar and CO₂ clusters, *J. Chem. Phys.*, 1997, **106**, 1402–1410.
- 33 U. Bhattacharjee, C. A. Chesta and R. G. Weiss, Temperature-dependent cage effects from triplet radical pairs generated upon irradiation of 1-(4-methylphenyl)-3-phenyl-2-propanone in polyethylene films, *Photochem. Photobiol. Sci.*, 2004, **3**, 287–295.
- 34 J. Franck and E. Rabinowitsch, Free radicals and the photochemistry of solutions, *Trans. Faraday Soc.*, 1934, **30**, 120–131.
- 35 E. Schutte, T. J. R. Weakley and D. R. Tyler, Radical Cage Effects in the Photochemical Degradation of Polymers: Effect of Radical Size and Mass on the Cage Recombination Efficiency of Radical Cage Pairs Generated Photochemically from the (CpCH₂CH₂N(CH₃)C(O)(CH₂_nCH₃Mo₂(CO)₆) (*n* = 3, 8, 18) Complexes, *J. Am. Chem. Soc.*, 2003, **125**, 10319–10326.
- 36 J. D. Harris, A. B. Oelkers and D. R. Tyler, The Solvent Cage Effect: Is There a Spin Barrier to Recombination of Transition Metal Radicals?, *J. Am. Chem. Soc.*, 2007, **129**, 6255–6262.
- 37 J. D. Harris, A. B. Oelkers and D. R. Tyler, Microviscosity and wavelength effects on radical cage pair recombination, *J. Organomet. Chem.*, 2007, **692**, 3261–3266.
- 38 N. Nodelman and J. C. Martin, Solvent cage effect in the photolysis of azomethane in aqueous alcohols and other media: a semiempirical correlation with macroscopic solvent parameters, *J. Am. Chem. Soc.*, 1976, **98**, 6597–6608.
- 39 A. B. Oelkers, L. F. Scatena and D. R. Tyler, Femtosecond pump–probe transient absorption study of the photolysis of [Cp′Mo(CO)₃]₂ (Cp′ = η⁵-C₅H₄CH₃): Role of translational and rotational diffusion in the radical cage effect, *J. Phys. Chem. A*, 2007, **111**, 5353–5360.
- 40 D. A. Braden, E. E. Parrack and D. R. Tyler, Photochemical studies as a function of solvent viscosity. A new photochemical pathway in the reaction of (η⁵-C₅H₄Me)₂Mo₂(CO)₆ with CCl₄, *Photochem. Photobiol. Sci.*, 2002, **1**, 418–420.
- 41 R. M. Noyes, Kinetics of competitive processes when reactive fragments are produced in pairs, *J. Am. Chem. Soc.*, 1955, **77**, 2042–2045.
- 42 T. Koenig and H. Fischer, Cage effects, *Free Radicals*, 1973, **1**, 157–189.
- 43 A. R. Manning, P. Hackett, R. Birdwhistell and P. Soye, Hexacarbonylbis(η⁵-cyclopentadienyl)dichromium, molybdenum, and tungsten and their analogs, M₂(η⁵-C₅H₄R)₂(CO)₆ (M = Cr, Mo, and W; R = H, Me or PhCH₃), *Inorg. Synth.*, 1990, **28**, 148–150.
- 44 D. A. Braden, E. E. Parrack and D. R. Tyler, 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?, *Coord. Chem. Rev.*, 2001, **211**, 279–294.
- 45 J. L. Male, B. E. Lindfors, K. J. Covert and D. R. Tyler, Cage Effects in the Photochemical Degradation of Polymers. Studies of Model Complexes with Different Chain Lengths, *Macromolecules*, 1997, **30**, 6404–6406.
- 46 A. B. Oelkers, E. J. Schutte and D. R. Tyler, Solvent Cage Effects: The Influence of Radical Mass and Volume on the Recombination Dynamics of Radical Cage Pairs Generated by Photolysis of [CpCH₂CH₂N(CH₃)C(O)(CH₂_nCH₃Mo(CO)₃]₂ (*n* = 3, 8, 13, 18) (Cp = η⁵-C₅H₄) Complexes, *Photochem. Photobiol. Sci.*, 2008, **7**, 228–234.