transfer of an electron to the arene is unknown but may be facilitated by a bridging iodide as suggested by Kumada in his Ni-catalyzed synthesis of biphenyls.[13] Kochi has suggested an electron-transfer mechanism for halide exchange of arenes in nonpolar solvents.[14]

The mechanism suggests that NiX_4^{2-} is a reducing agent for chloroarenes. Accordingly, we have performed some preliminary electrochemical measurements on the $NiBr_2$ system. All measurements were performed in DMF at a Pt disk-working electrode against a silver wire reference. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium tetrafluoroborate, and the concentration of the substrate was 0.005 M. Cyclic voltammetry at 100 mV/s sweep rate indicates an oxidation wave for solutions of $NiBr_2$ and NaI that does not appear in the cyclic voltammogram of either component separately. While not unequivocal, this observation is consistent with the formation of a better reducing agent in solution upon interaction of $NiBr_2$ and NaI. The nature and reducing ability of this species is unknown. Mechanistic study and application of this new method to the synthesis of other systems is underway.

Acknowledgment. We thank Professor Martin F. Semmelhack for stimulating discussions. The assistance of Dr. Patrick Kinlen of Monsanto's Corporate Research and Development Staff with the electrochemical measurements is greatly appreciated.

---

(12) (a) Bunnett, J. F.; Sundberg, J. E. *Chem. Pharm. Bull.* **1975**, *23*, 2620. (b) Rossi, R. A.; deRossi, R. A.; Lopez, A. F. *J. Org. Chem.* **1976**, *41*, 3371.

(13) Zembayashi, M.; Tamao, K.; Yoshida, J.; Kumada, M. *Tetrahedron Lett.* **1977**, 4089.

(14) Tsou, T. T.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 1930.

The Cage Effect and Apparent Activation Parameters for Bond Homolysis

T. Koenig* and R. G. Finke*

Department of Chemistry, University of Oregon
Eugene, Oregon 97403-1210

Received October 26, 1987

A number of recent[1-5] results demonstrate that transition metal carbon bond homolyses occur in solution at only slightly elevated temperatures. Up until now, these important observations have been interpreted[1-6] in terms of models[1] that do not include the effects of the cage pair intermediate which is unique to solution phase studies (Scheme I, Figure 1). We wish to point out that, as has been demonstrated with organic peroxides,[6-9] the cage effect must be considered in M–L bond homolyses in solution. We provide here a set of equations that will help clarify the connection between observed activation parameters ($\Delta H^{\ddagger}_{\rm obsd}$ and $\Delta S^{\ddagger}_{\rm obsd}$) and those for the homolytic elementary step in solution ($\Delta H^{\ddagger}_1(\rm s)$, $\Delta S^{\ddagger}_1(\rm s)$). These equations, while straightforward, have not been previously emphasized in the cage literature. They are especially significant for M–L systems, many of which cannot be studied in the gas phase where bond dissociation is not complicated by the cage effect. The formalism provided here is therefore of considerable current interest.

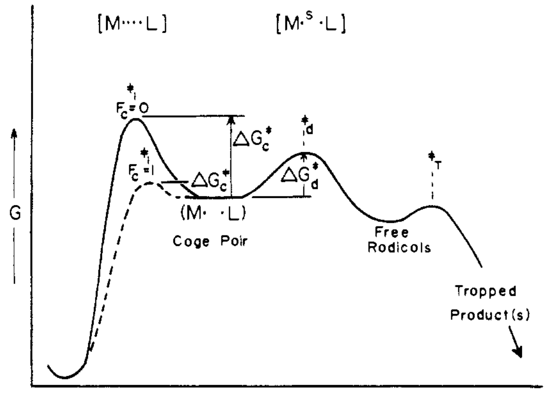


Figure 1.

Scheme I shows the phenomenological version of our cage effect model,[6] cast in terms of a metal–carbon (M–L) bond homolysis. The free-energy diagram, corresponding to this scheme, is shown in Figure 1 where the two limiting cases ($k_d \gg k_c$, solid line and $k_c \gg k_d$, dashed line) are indicated. The k_{-1} of Scheme I is the rate constant for recombination of *free radicals* to form the cage pair. The rate constant designated k_c is for cage pair combination and is expected to be greater than k_{-1} ($k_c \neq k_{-1}$). The k_d step in Scheme I is meant to describe the diffusive disappearance of the cage pair and is also *not*, in general, expected to be equal to k_{-1}.[10a]

Scheme I defines k_1 as the rate constant for the formation of the *cage pair in solution.* The k_T process of Scheme I designates the reaction of one or both of the *free radicals* (M$^{\bullet}$, L$^{\bullet}$) with a

---

(1) (a) Halpern, J. *Pure Appl. Chem.* **1979**, *51*, 2171. Halpern, J. *Pure Appl. Chem.* **1983**, *55*, 1059. Halpern, J. *Pure Appl. Chem.* **1986**, *58*, 575. (b) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238. (c) Halpern, J.; Ng, F. T. T.; Rempel G. L. *J. Am. Chem. Soc.* **1979**, *101*, 7124. (d) Ng, F. T. T.; Rempel, G. L.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 621. (e) Tsou, T. T.; Loots, M.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 623. (f) Ng, F. T. T.; Rempel, G. L.; Halpern, J. *Inorg. Chim. Acta* **1983**, *77*, L165. (g) Halpern, J.; Kim, S.-H.; Leung, T. W. *J. Am. Chem. Soc.* **1984**, *106*, 8317. (h) Geno, M. K.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1238. (i) Geno, M. K.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1052.

(2) (a) Finke, R. G.; Smith, B. L.; Mayer, B. J.; Molinero, A. A. *Inorg. Chem.* **1983**, *22*, 3677. (b) Finke, R. G.; Hay, B. P. *Inorg. Chem.* **1984**, *23*, 3041. (c) Hay, B. P.; Finke, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4820. (d) Hay, B. P.; Finke, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 8012. (e) Finke, R. G.; Waddington, M., submitted for publication. (f) Koenig, T.; Hay, B. P.; Finke, R. G. *Polyhedron*, in press.

(3) Collman, J. P.; McElwee-White, L.; Brothers, P. J.; Rose, E. *J. Am. Chem. Soc.* **1986**, *108*, 1332.

(4) Ohgo, Y.; Orisaku, K.; Hasegawa, E.; Takeuchi, S. *Chem. Lett.* **1986**, 27.

(5) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5197. Gjerde, H. B.; Espenson, J. H. *Organometallics* **1982**, *1*, 435. Blau, R. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 3530.

(6) (a) Koenig, T. In *Free Radicals*; Kochi, J., Ed.; John Wiley: New York, 1973; Vol. 1, Chapter 3. (b) Koenig, T.; Fischer, H. In *Free Radicalsf* Kochi, J., Ed.; John Wiley: New York, 1973; Vol. 1, Chapter 4. (c) Koenig, T. In *Organic Free Radicals*; Pryor, W. A., Ed.; *ACS Symposium Series 69*; 1978; Chapter 9 and references therein. (d) Koenig, T.; Hoobler, J. A. *Tetrahedron Lett.* **1972**, 1803. (e) Owens, J.; Koenig, T. *J. Org. Chem.* **1974**, *39*, 3153. (f) Koenig, T.; Owens, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4052.

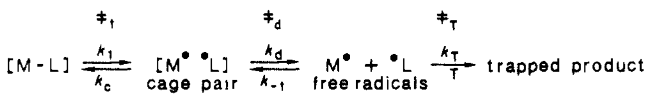
(7) Neuman, R. C., Jr. *Acc. Chem. Res.* **1972**, *5*, 381.

(8) Pryor, W. A.; Smith, K. *J. Am. Chem. Soc.* **1970**, *92*, 5403.

(9) Martin, J. C.; Dombchik, S. A. *Adv. Chem. Ser.* **1968**, no. 75, 269. Martin, J. C.; Nodelman, N. *J. Am. Chem. Soc.* **1976**, *98*, 6597–6608.

(10) (a) The value of k_{-1} and $\Delta H^{\ddagger}_{-1}$ in the gas phase must also be kept distinct from $\Delta H^{\ddagger}_{-1}$, $\Delta H^{\ddagger}_d$, and $\Delta H^{\ddagger}_c$ in solution. For simplicity, recombination is the only *chemical* cage reaction that we have included in Scheme I. Disproportionations, etc. could be included[6] and in fact are probable for M–L systems with β–hydrogens.[2f] (b) The suggestion,[1] widely employed[2-5] prior to the availability of eq 2 and 3 herein, that bond dissociation energies can be obtained by simply subtracting the activation enthalpy for a diffusion-controlled reaction in the solvent in which $\Delta H^{\ddagger}_{\rm obsd}$ was measured ($\Delta H^{\ddagger}_{-1} \sim 2$ kcal/mol for acetone or toluene) requires the implicit assumptions that $F_c \sim 1$ and that solvation effects are not important. Most literature estimates of F_c are not this large in fluid solvents such as those used for the $\Delta H^{\ddagger}_{\rm obsd}$ determinations. However, most quantitative values for F_c come from cage pairs with intervening small molecules. Higher F_c values are possible in M–L systems where no small molecule is formed in the homolytic event. A high value of F_c means that the rate determining transition state is $\ddagger_d$ (Figure 1); $\ddagger_d$ is well removed from $\ddagger_1$ and is subject to medium effects in addition to M·, L· structural effects. Schemes[1] that do not recognize the cage pair intermediate will not be able to separate these effects. (c) The activation entropy associated with eq 1, defined $\ln(k_{\rm obsd}/T)$ as T goes to infinity is $\Delta S^{\ddagger}_{\infty} = \Delta S^{\ddagger}_1(\rm s) - R\cdot\ln\{1 + \exp[(\Delta S^{\ddagger}_c - \Delta S^{\ddagger}_d)/R]\}$. This definition does not apply except at $T \rightarrow \infty$. (d) This approximation rests on *purely numerical* results and is quite distinct from the *analytic expression* for $\Delta H^{\ddagger}_{\rm obsd}$ (eq 2). It is accurate outside of the $0.1 < F_c < 0.9$ interval and is otherwise good to about ±2 eu. $\Delta S^{\ddagger}_{\rm obsd}$ does not have as good a definition as usual unless F_c is a constant over the temperature range used for the $k_{\rm obsd}$ measurements.

Scheme I



radical trap (T) such as DPPH,[6f] TEMPO,[1,2] or an efficient hydrogen donor.[11] Under conditions where the trap (T) is present in modest concentrations[11a] (~0.1 M) and in excess of [M–L], the observated rate constant (k_{obsd}) for the homolysis process will be given by eq 1. The term in brackets is the complement of the

$$k_{obsd} = [1 - F_c]\cdot k_1 \qquad (1)$$

$$F_c = k_c/(k_c + k_d) \qquad (1a)$$

fractional cage efficiency, F_c, which is defined as shown in eq 1a. Taking the first derivative of k_{obsd} (eq 1) with respect to T^{-1} yields eq 2. Here $\Delta H^{\ddagger}_{obsd}$ is the usual $\ln(k_{obsd}/T)/(1/T)$ slope, $\Delta H^{\ddagger}_1(s)$

$$\Delta H^{\ddagger}_{obsd} = \Delta H^{\ddagger}_1(s) + F_c\cdot[\Delta H^{\ddagger}_d - \Delta H^{\ddagger}_c] \qquad (2)$$

is the activation enthalpy for the k_1 step *in solution*, while $\Delta H^{\ddagger}_d$ and $\Delta H^{\ddagger}_c$ are the steps in Scheme I that are unique to the solution phase where the cage intermediate pertains. Equation 2 is quite important in showing the proper connection between $\Delta H^{\ddagger}_{obsd}$ and $\Delta H^{\ddagger}_1(s)$. It reveals that F_c, $\Delta H^{\ddagger}_d$, and $\Delta H^{\ddagger}_c$ but not $\Delta H^{\ddagger}_{-1}$ could be corrections in obtaining $\Delta H^{\ddagger}_1(s)$ from $\Delta H^{\ddagger}_{obsd}$.[10b]

The relationship between the observed[10c,d] activation entropies and those for the elementary steps of Scheme I is given in eq 3. The $\Delta S^{\ddagger}_d - \Delta S^{\ddagger}_c$ term could be a substantial part of $\Delta S^{\ddagger}_{obsd}$ depending on F_c.

$$\Delta S^{\ddagger}_{obsd} \simeq \Delta S^{\ddagger}_1(s) + F_c\cdot[\Delta S^{\ddagger}_d - \Delta S^{\ddagger}_c] \qquad (3)$$

Equations 2 and 3 make it clear that the cage efficiency factor, F_c, is a variable that must be considered. The value of F_c certainly changes with changing solvent, temperature, and M–L structure. No experimental data on even an approximate F_c value for any M–L bond homolyses, much less its variation, have been provided as yet. There is a continuum between $F_c \sim 0$ ($\Delta G^{\ddagger}_c$ higher than $\Delta G^{\ddagger}_d$) and $F_c \sim 1.0$ ($\Delta G^{\ddagger}_c$ lower than $\Delta G^{\ddagger}_d$ (Figure 1)), and it is not known, at the present time, where M–L systems fit into this spectrum.

Equation 1 teaches that measurement of both k_{obsd} and F_c at several temperatures will give k_1 and hence $\Delta H^{\ddagger}_1(s)$ directly without the complication of $\Delta H^{\ddagger}_d - \Delta H^{\ddagger}_c$ (at least within the confines of Scheme I). Oxygen-18 scrambling studies for peresters are cases where eq 1 has been used to estimate the cage effect. In M–L homolysis, the equivalent measurement could be the rate of racemization of an M–L having a chiral carbon ligand. If either the molecular tumbling[6f,13,16–20] of the carbon radical with respect to the M· or an appropriate internal rotation[6f] in the carbon radical (at the cage pair stage) were much faster than k_c, then the rate constant for racemization would give k_1 of Scheme I directly. The cage effect would be evident in a lower value for k_{obsd} under the same conditions.[15] However, the precedents from the organic literature show that some retention of oxygen-18 label[6c] or carbon configuration[6f,16–20] are the result for cage combination, even for systems in which F_c is small. If organometallic systems do exhibit high F_c values, as has been implicitly assumed[10b] in recent work on M–L systems, then racemization rates might not count every homolytic event.[15a]

Finally, we should like to point out that a cage pair is effectively a diradical and, as Houk[21] has shown for the carbene–olefin reaction and Doubleday[22] has discussed for 1,4-diradicals, the activation enthalpy for bond formation, corresponding to k_c of Scheme I, *can be negative*. A negative value for $\Delta H^{\ddagger}_c$ is quite possible and simply requires that $\Delta S^{\ddagger}_c$ be sufficiently negative to make $\Delta G^{\ddagger}_c$ positive.[23] Equations 2 and 3 teach that negative values for $\Delta H^{\ddagger}_c$ and $\Delta S^{\ddagger}_c$ increase the cage effect contribution to $\Delta H^{\ddagger}_{obsd}$ and $\Delta S^{\ddagger}_{obsd}$ since they reinforce the positive values of $\Delta H^{\ddagger}_d$ and $\Delta S^{\ddagger}_d$.

In summary, we have provided an improved set of relationships for evaluating apparent activation parameters for M–L and other dissociation processes in solution. The equations make it clear that attention to the cage effect is mandatory before any final interpretation of variations in $\Delta H^{\ddagger}_{obsd}$ and $\Delta S^{\ddagger}_{obsd}$ for M–L bond homolysis is possible. The equations presented here set the stage for the evaluation of bond dissociation energies derived from solution phase kinetics. The connections between $\Delta H_1^{\ddagger}(s)$ and bond dissociation energies involve an additional set of considerations which are treated elsewhere.[2f]

Acknowledgment. This work was supported in part by the National Science Foundation (CHE 8419950, Thomas Koenig) and by the NIH (DK-26214, Richard G. Finke). It is a pleasure to acknowledge the helpful comments of Professor David Tyler.

---

(11) (a) Waits, H. P.; Hammond, G. S.; *J. Am. Chem. Soc.* **1964**, *86*, 1911. (b) At high (1–10 M) concentrations, the trap can be part of the cage wall with different effects[12–14] than those treated here.

(12) Skell, P. S.; Baxter III, H. N.; Tanko, J. M.; Chebolu, V. *J. Am. Chem. Soc.* **1986**, *108*, 6300. Skell, P. S.; Baxter III, H. N. *J. Am. Chem. Soc.* **1985**, *107*, 2823.

(13) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Lusztyk, J.; Sciano, J. C. *J. Am. Chem. Soc.*, **1985**, *107*, 5464–5472.

(14) Bunce, N. J.; Joy, R. B.; Landers, J. P.; Nakai, J. S. *J. Org. Chem.* **1987**, *52*, 1155.

(15) (a) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.*, **1986**, *108*, 4679–4681. (b) The interpretation given in the recent report[15a] of activation parameters for racemization of a chiral Rh–C system contains the conditions of 10b *and* the implicit assumption that no racemization process can occur in the cage pair. The high implied F_c value ($F_c = 1$) could be due to a high k_c value so that rotational motions at the cage pair stage do not compete. However, a high F_c value can also arise from a low k_d, and thus the $\Delta H^{\ddagger}_1(s)$ value for this system is not really known at present.

(16) Doering, W. von E.; Birladeanu, L. *J. Am. Chem. Soc.* **1986**, *108*, 7442–7444.

(17) Kopecky, K. R.; Gillan, T. *Can. J. Chem.* **1969**, *47*, 2371–2386.

(18) Greene, F. D., Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867.

(19) Lee, K.-W.; Horowitz, N.; Ware, J.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 2622.

(20) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2463–2481. Lehni, M.; Fischer, H. *Int. J. Chem. Kin.* **1983**, *15*, 733–757. Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1984**, *88*, 2555–2559.

(21) Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 4293.

(22) Doubleday, C., Jr.; Camp, R. N.; King, H. F.; McIver, J. W.; Mullally, D.; Page, M. *J. Am. Chem. Soc.* **1984**, *106*, 447.

(23) The value of $\Delta H^{\ddagger}_c$ could be negative and substantial in associated solvents if formation of the cage pair disrupts solvent–solvent stabilization.

---

^{6}Li, ^{13}C, and ^{15}N NMR Spectroscopic Studies of Lithium Dialkylamides. Solution Structure of Lithium Isopropylcyclohexylamide (LICA) in Tetrahydrofuran

Angela S. Galiano-Roth, Elias M. Michaelides, and
David B. Collum*

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853-1301

Received November 2, 1987

Lithium dialkylamides have played a prominent role in the development of carbon–carbon bond-forming reactions.[1] Nevertheless, our understanding of dialkylamide solution structures relies heavily on indirect methods such as analogy with solid-state structures[2–7] or with solution structures of more-or-less related

---

(1) Stowell, J. C. *Carbanions in Organic Synthesis*; Wiley: New York, 1979. Jackman, L. M.; Lange, B. C. *Tetrahedron* **1977**, *33*, 2737. d'Angelo, J. *Tetrahedron* **1976**, *32*, 2979. House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: New York, 1972.

(2) (a) Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 5539. (b) Williard, P. G.; Salvino, J. M. *J. Am. Chem. Soc.* **1988**, in press. (c) Armstrong, D. R.; Barr, D.; Clegg, W.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 869.

(3) Reed, D.; Barr, D.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Dalton Trans.* **1986**, 557.

(4) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 285.

(5) Rogers, R. D.; Atwood, J. L.; Grüning, R. *J. Organomet. Chem.* **1978**, *157*, 229. Mootz, D.; Zinnius, A.; Böttcher, B. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 378. Lappert, M. F.; Slade, M. J.; Singh, A.; Atwood, J. D.; Rogers, R. D.; Shakir, R. *J. Am. Chem. Soc.* **1983**, *105*, 302.

0002-7863/88/1510-2658$01.50/0