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Empirical Approach to Substituent Effects in [3,3]-Sigmatropic Shifts Utilizing the Thermochemistry of Coupled Nonconcerted Alternative Paths

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Substituents affect the structure of the [3,3]-sigmatropic shift transition state as deduced from α secondary deuterium kinetic isotope effects. Since this variation is interpretable in terms of the relative stability of bond breaking and bond making nonconcerted alternatives as suggested by Thornton, an attempt is made to correlate the rates of these reactions with the free energies of formation of the transition state for nonconcerted bond breaking (BB) and bond making (BM) and with the free energy of reaction. Two correlation equations (eq 4 and 8) are derived from hyperbolic paraboloid models of the energy surface; in each the activation free energy is the harmonic mean of $\Delta G^{\ddagger}$BB and $\Delta G^{\ddagger}$BM modified by ΔG_r and weighted by a constant which relates to the extent of coupling of the nonconcerted alternatives, i.e., the degree of concert. These are applied to chairlike and boatlike [3,3] shifts and to the aliphatic Claisen rearrangement.

Correlation, let alone prediction, of rate responses to different substituents on systems undergoing a concerted pericyclic reaction represents a substantial problem. In principle, quantum chemistry can provide such information, but the current state of good calculations is such that only small molecular systems can be analyzed at reasonable costs. Attempts by Carpenter and Wilcox, utilizing simple Hückel theory, have had remarkable success with electrocyclic reactions.[1] However, the [3,3]-sigmatropic shift and the Diels–Alder cycloaddition are more problematical. The difficulties in this approach probably arise from variation in transition-state structure in response to substitution. Although semiempirical and perturbation MO methods have been used to correlate substituent effects on rates, particularly in cycloaddition reactions[2] but also in sigmatropic shifts,[3] information about the transition-state structure can only be obtained by a complete calculation of the potential energy surface for each substituent.

The idea that transition-state structure in concerted reactions changes with substituents is not a novel one.[4] Indeed, it would appear that in any concerted reaction, where bonds are made and broken simultaneously, the extent of bond making and bond breaking might be expected to respond differently to substituents. Two effects have been identified by Thornton[5] as being responsible for the variation: the perpendicular effect which arises by changes in force constants of vibrations other than those that become part of the reaction coordinate and the parallel or reaction coordinate effect which is an extension of the Hammond postulate.[6] In [3,3]-sigmatropic shifts, the change in the ratio of the secondary kinetic isotope effects (KIE) on bond making at C-1 and C-6 with respect to those for bond breaking at C-3 and C-4 and the change in these with respect to equilibrium isotope effects (EIE) as a function of substituents are highly suggestive of a variable transition-state structure.[7] A More O'Ferrall–Jencks (MOF-J) diagram[4b,c] of the [3,3]-sigmatropic shift compactly illustrates the data. It provides a structural interpretation of the transition state if the coordinates ln KIE/ln EIE, which may be regarded as reaction indices,[8] are nearly linearly related to bond order changes[9] (see Figure 1). The MOF-J diagrams have previously been used to represent elimination reactions and carbonyl addition reactions.[4] In these cases, the structural coordinates were considered to be reaction indices like the Brønsted α and β_{nuc}.

In order to correlate rate changes in concerted reactions, calculation of the MOF-J energy surface would be of inestimable value, but even the potential functions that represent the structural coordinates of the MOF-J energy surface (the edges of the MOF-J diagram) must be complex, since these coordinates are combinations of changes in a number of normal coordinate vibrations. Nonetheless, since the relative energies of the species at the four corners can be determined or reasonably estimated from thermochemical addivity,[10] a simple model equation that could describe the MOF-J surface was examined. One, a hyperbolic paraboloid, was used to generate a nonlinear equation that could roughly correlate the activation free energy with changes in the free energies of the species at the four corners. This correlation equation was communicated previously with necessarily incomplete discussion of its origins, applicability, and limitations.[7b] The model has been critized[11] for these failures; therefore, a full paper describing the model and appropriate extensions is in order.[12]

Experimental Background

Kinetic studies of the [3,3]-sigmatropic shift in a number of substituted 1,5-dienes provide appropriate background for consideration of rate correlation equations. Substitu-

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[1] Wilcox, C., Jr.; Carpenter, B. K. *J. Am. Chem. Soc.* **1979**, *101*, 3897.

[2] For reviews see: Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: London, 1976. Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 799.

[3] Epiotis, N. D.; Shaik, S. *J. Am. Chem. Soc.* **1977**, *99*, 4936.

[4] (a) Bunnett, J. F. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 225. (b) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274. (c) Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705; *Acc. Chem. Res.* **1980**, *13*, 161.

[5] Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915.

[6] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

[7] (a) Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142. (b) *J. Am. Chem. Soc.* **1979**, *101*, 4393.

[8] Winey, D. A.; Thornton, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 3102.

[9] There are suggestions that this reaction index is linear in bond order: Buddenbaum, W.; Shiner, V. J., Jr. In "Isotope Effects in Enzyme Catalyzed Reactions"; University Press: Baltimore, MD, 1977. There are also suggestions to the contrary: Humski, K.; Malojčič, R.; Borčič, S.; Sunko, D. E. *J. Am. Chem. Soc.* **1970**, *92*, 6534.

[10] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

[11] (a) Burrows, C. J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 6984. (b) Our early communication assumed that the product was at a point (p,p) to introduce the scaling factor; this leads to an equation like eq 4 but where ΔG_r is divided by p.[7] For a pictoral description of this surface, see: Lowry, T. H.; Schueller Richardson, K. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; pp 886–7.

[12] Murdoch, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 2660. See this paper for a correlation model based on surfaces with quadratic edge potential and Marcus Theory which is closely related to work described here.

0022-3263/84/1949-0011$01.50/0

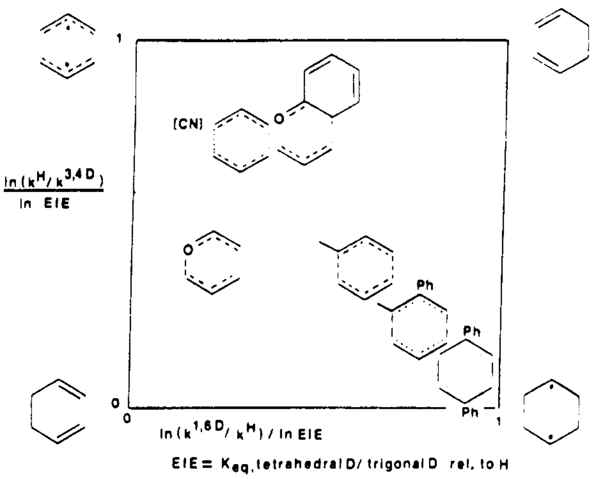

Figure 1.

tion of radical-stabilizing groups, particularly phenyl groups, at C-2 and C-5 led to rate enhancements of approximately 50×/phenyl.[13] While these effects were interpreted in terms of sole involvement of the 1,4-cyclohexanediyl intermediate, energetic considerations render this interpretation unlikely. Phenyl stabilization of radicals is substantial (~15 kcal/mol),[10] and since a double bond is stabilized by only ~5 kcal/mol by a conjugating phenyl group, the rate enhancement should have been of the order of 10^5×/phenyl for a 1,4-cyclohexanediyl intermediate. Similar observations have been made with phenyl substitution at C-3 and C-4. The implication of these data is that the effects of radical-stabilizing substituents are attenuated in the transition state for this rearrangement.

Correlation Equations

Energy surfaces cast in units of enthalpy changes have the virtue that they are relatively independent of temperature. However, the rates of reactions are critically dependent on entropy changes. Further, the activation parameters of reactions reflect different entropy changes, depending on the structure of the transition state: witness the very low preexponential term for the [3,3] shift of 2,5-diphenyl-1,5-hexadiene ($10^{8.86}$ s^{-1})[13] while the *A* factor for boat [3,3] shifts is typically 10^{13} s^{-1}.[14] It would appear that any correlation equation of rates must deal with these enormous activation entropy differences. Another example of how misleading enthalpy changes alone can be may be found in Dewar's work on the phenyl-substituted 1,5-hexadienes. The relative rates of unsubstituted, 2-phenyl-, and 2,5-diphenyl-1,5-hexadienes are 1:50:2500 at 250 °C, but the $\Delta H^{\ddagger}$'s are 33.5, 29.3, and 21.2 kcal/mol, respectively; of course, the log *A*'s which are 10.26, 10.92, and 8.86, respectively, compensate for these differences.[15]

One of the assumptions behind the correlation described below, therefore, is that entropy changes have mechanistic significance. Consideration of the $\Delta S^{\ddagger}$'s for the bond breaking nonconcerted alternative and the bond making nonconcerted alternative in the [3,3] shift reveals a large difference, as would be expected, so any interpolation between these two alternatives must utilize $\Delta G^{\ddagger}$'s at a given temperature. Of course, ΔS's themselves increase with increasing temperatures. However, ΔS's change generally by only 20%, on going from 300 to 600 K,[10] and so comparison of $\Delta S^{\ddagger}$'s from reactions with over a 200 K range of temperatures, say from 400 to 600 K as in the [3,3] shift, will not introduce a large error in the estimates.

MOF-J analysis and the experimental results discussed above suggest that quantification of substituent effects on the [3,3] shift might be found in the relationship between the activation free energies for scission to two allyl radicals ($\Delta G^{\ddagger}_y$) and for formation of cyclohexane-1,4-diyl ($\Delta G^{\ddagger}_x$) and the free energy of reaction (ΔG_r). This relationship

$$\Delta G^{\ddagger} = f(\Delta G^{\ddagger}_x, \Delta G^{\ddagger}_y, \Delta G_r)$$

might be provided by knowledge of the energy surface, particularly if the two structural coordinates of the surface were confined to values between 0 and 1 as in most reactivity indices.[8]

Model I. The simplest equation for a surface with a saddle point is eq 1, where the constants may be fixed if

$$\Delta G = ax + by + cxy + d \tag{1}$$

the surface is constrained to $x,y = 0 \rightarrow 1$. Making the assumption that the $\Delta G^{\ddagger}$'s for formation of two allyl radicals and for formation of cyclohexane-1,4-diyl are at the points (0,1) and (1,0), respectively, $a = \Delta G^{\ddagger}_x$ and $b = \Delta G^{\ddagger}_y$. If the product is located at point (1,1), then $c = \Delta G_r - \Delta G^{\ddagger}_x$ $\Delta G^{\ddagger}_y$. The saddle point of the surface equation (eq 1) can be determined by setting the partial derivatives of eq 1 equal to zero.[18] This gives the relationships of eq 2, which

$$x^{\ddagger} = -b/c \qquad y^{\ddagger} = -a/c \tag{2}$$

after substitution in eq 1, with the definitions of the constants above, give eq 3.

$$\Delta G^{\ddagger} = \frac{\Delta G^{\ddagger}_x \, \Delta G^{\ddagger}_y}{\Delta G^{\ddagger}_x + \Delta G^{\ddagger}_y - \Delta G_r} \tag{3}$$

Remarkably, eq 3 provides a good correlation ($r = 0.97$) of the experimental data of Table I on chairlike [3,3] shifts where the energies of the nonconcerted paths have been either determined or estimated by thermochemical kinetics.[10] These estimates will be discussed subsequently.

There are several interesting aspects of this simple model. The activation energy is calculated to be the harmonic mean of the transition-state energies of the nonconcerted alternatives modified by ΔG_r in a reasonable manner; that is, the more negative (exergonic) ΔG_r is, the

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(13) Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1972**, *94*, 7147. Shea, K. J.; Phillips, R. B. *Ibid.* **1980**, *102*, 3156.

(14) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 7147. Shea, K. J.; Phillips, R. B. *Ibid.* **1980**, *102*, 3156.

(15) Two reviewers objected to the use of $\Delta G^{\ddagger}$ rather than $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ separately. One wrote, "The hazards of lumping together (as in Hammett plots) are well-known and have been forcefully presented by Kwart." The reader will recognize that it is also well-known that the problems arise only near the isokinetic temperature, and with the normal range of activation parameters for the [3,3] shifts, the calculated isokinetic temperature is approximately 1500 K. Thus relative $\Delta G^{\ddagger}$'s at a single temperature (arbitrarily 250 °C) are sufficient to characterize [3,3] shifts over the usual range of temperatures.

(16) $\Delta G^{\ddagger}$ for first order formation of two allyl radicals from 1,5-hexadiene has been determined experimentally: Golden, D. M.; Gac, N. A.; Benson, S. W. *J. Am. Chem. Soc.* **1969**, *91*, 2136. Note that the species at (0,1) on our surfaces is the transition state for formation of two allyl radicals.

(17) Previous analyses of the [3,3]-shift energy surface suggested that cyclohexane-1,4-diyl is separated from 1,5-hexadiene by a kinetic barrier of 53 kcal/mol at 250 °C. If the diyl has a barrier to cleavage back to 1,5-hexadiene, then this barrier should occur on the energy surface. It is assumed here that the transition state in this highly exergonic reaction cleavage so resembles the diyl that the transition state reaction indices are approximately those for making the diyl.

(18) Equation 1 fails the second derivative test, i.e., $\partial^2\Delta G/\partial x^2 = 0 = \partial^2\Delta G/\partial y^2$, but this is merely an artifact of the choice of coordinates. A 45° coordinate rotation gives an equation whose second derivatives are finite; further, the saddle point position is the same as that calculated from the first derivative of eq 1. The coordinate system used was chosen because of its correspondence to α secondary deuterium isotope effects[7] and chemists' affinity for reaction indices between 0.0 and 1.0. The irrelevance of the lack of stationary points for reactant, product, and nonconcerted alternatives on the surfaces described here has been discussed by Murdoch.[12]

Table I. $\Delta G^{\ddagger}$'s of [3,3]-Sigmatropic Shifts at 523 K

reactant	$\Delta G^{\ddagger}{}_y{}^{a,l}$ (C-3,C-4 fission)	$\Delta G^{\ddagger}{}_x{}^{a,l}$ (C-1,C-6 formation)	$\Delta G_r{}^{a,l}$	$\Delta G^{\ddagger}{}_{xp}{}^{l}$	$\Delta G^{\ddagger}{}_{calcd}{}^{l}$		
					eq 8 ($a = -27$ kcal/mol)	eq 3	eq 4 ($p = 1.5$)
1,5-hexadiene (chair)	57[b]	53[b]	0	41[c]	40.9	27.5	41
2-phenyl-1,5-hexadiene	57	43	0	35.5[d]	37.4	24.5	36.5
3-phenyl-1,5-hexadiene	47	53	−5	37.5[d]	37.1	23.7	36
2,5-diphenyl-1,5-hexadiene	57	33	0	31[d]	32	20.9	31
2,5-dicyano-3-methyl-1,5-hexadiene	54	33	−3	31[e]	31.5	19.8	30
threo-3,4-dimethyl-1,5-hexadiene	53	53	−5	39[f]	38.8	25.3	38
threo-3,4-diphenyl-1,5-hexadiene	37	53	−10	31[g]	32.3	19.6	29
2,4-diphenyl-1,5-hexadiene	47	43	−5	34[d]	35.8	21.3	32
allyl vinyl ether	47	57	−17	33[h]	35.5	22.1	33
allyl phenyl ether	47	69	5	42[i]	41.7	29.2	44
allyl acetate	52	67	0	45[j]	42.4	29.3	44

[a] See Table II and the accompanying discussion for derivation of these values. [b] Reference 7. [c] Doering, W. von E.; Toscano, V. G.; Beasley, G. M. *Tetrahedron*, 1971, *27*, 5299. [d] Reference 13. [e] Wehrli, R.; Schmid, H.; Bellus, D. E.; Hansen, H.-J. *Helv. Chim. Acta* **1972**, *60*, 1365. [f] Doering, W. von E.; Roth, W. R. *Tetrahedron* **1962**, *18*, 67. [g] Lutz, R. P.; Berg, H. A. J. *J. Org. Chem.* **1980**, *45*, 3915. [h] Schuler, F. W.; Murphy, G. W. *J. Am. Chem. Soc.* **1950**, *72*, 3155. Reference 11. [i] For a review, see: Rhoads, S. J.; Rawlins, N. R. *Org. React.* **1975**, *22*, 1. [j] Lewis, E. J.; Hill, J. T.; Newman, E. R. *J. Am. Chem. Soc.* **1968**, *90*, 682. [l] Values given in kilocalories per mole.

lower $\Delta G^{\ddagger}$ is Equation 3 predicts the following effects of substituent stabilization on the activation energy: (1) if $\Delta G^{\ddagger}_x \simeq \Delta G^{\ddagger}_y$, then altering one of these values will have an attenuated effect on $\Delta G^{\ddagger}$; (2) if $\Delta G^{\ddagger}_x \ll \Delta G^{\ddagger}_y$, a change in $\Delta G^{\ddagger}_x$ will have a large effect on $\Delta G^{\ddagger}$. Conversely, changing $\Delta G^{\ddagger}_y$ will have only a negligible effect on $\Delta G^{\ddagger}$. These predications are in general accord with the experimental results.

Although a plot of $\Delta G^{\ddagger}_{calcd}$ (eq 3) vs. $\Delta G^{\ddagger}_{xp}$ (experimental) is linear with a slope of ~0.7 (intercept = −1.7), the absolute values of $\Delta G^{\ddagger}_{calcd}$ are considerably underestimated. This may be rectified by introducing a scaling parameter, p (eq 4). There is a good correspondence

$$\Delta G^{\ddagger}_{xp} = p\Delta G^{\ddagger} = \frac{p\Delta G^{\ddagger}_x \Delta G^{\ddagger}_y}{\Delta G^{\ddagger}_x + \Delta G^{\ddagger}_y - \Delta G_r} \qquad (4)$$

between calculated and experimental activation energies (average deviation 1 kcal/mol) with $p = 1.5$ for the chairlike [3.3]-shifts of Table I.

The data used in Table I ($\Delta G^{\ddagger}_x$, $\Delta G^{\ddagger}_y$, and ΔG_r) are derived from kinetic studies of gas-phase reactions and the application of thermochemical kinetics (see below). For the [3,3]-sigmatropic shift the energy of 1,4-cyclohexanediyl follows from a group additivity calculation of the $\Delta\Delta G_f{}^{523}$ between bicyclo[2.2.0]hexane and 1,5-hexadiene and from the $\Delta G^{\ddagger}$ for the cleavage of bicyclo[2.2.0]hexane to 1,5-hexadiene, a reaction most likely involving 1,4-cyclohexanediyl.[9a,19] The $\Delta G^{\ddagger}$ for cleavage to two allyl radicals is obtained by extrapolating the experimentally determined activation parameters to 250 °C, the standard temperature used in the calculations of [3,3] shifts reported here. Application of the methods of thermochemical kinetics and, in particular, the radical stabilization energies of the substituents (vide infra) permits calculation of the remaining $\Delta G^{\ddagger}_x$ and $\Delta G^{\ddagger}_y$. For other pericyclic reactions the scaling factor p may well be different. In general, the larger p is, the less coupled are the nonconcerted alternatives, i.e., the less "concerted", the reaction is. For a thermoneutral pericyclic reaction, a p value approaching 2 would indicate a nonconcerted reaction.[20]

Despite the success of the model I, in correlation of data there are problems. Equation 4 violates microscopic reversibility in that the energy of the transition state (TS) is not the same for the forward and reverse reactions, although for exergonicities less than 10 kcal/mol, the deviations are small (~1–2 kcal/mol) Equation 3 does not violate microscopic reversibility, which indicates that the problem arises from introduction of the scaling factor.

Returning to the surface described by eq 3, consideration of its behavior reveals that the height of the saddle point is too low, relative to $\Delta G^{\ddagger}_y$ and $\Delta G^{\ddagger}_x$; thus this surface overestimates the extent of coupling of the noncentered alternatives. Another concern about this particular model is that neither the reactant nor the product represents a stationary point on the surface. Thus, the surface is not a realistic model for a chemical system. Nonetheless, since the object is to determine the height of the saddle point relative to that of the four corners by using relatively simple potential functions, the behavior at the reactant and product structures will be ignored even in the more sophisticated model equation described below. A final concern about this model is that it does not simplify to a simple edge potential for a nonconcerted reaction because of the scaling factor; thus, it cannot correlate the larger substituent effects expected for this type of reaction.[21]

Model II. In order to avoid the external scaling factor of eq 4, it became clear to us that introduction of quadratic terms into eq 1 could give a correlation equation which has an internal scaling factor. Equation 5 was used previously

$$\Delta G = ax^2 + by^2 + cxy + dx + ey + f \qquad (5)$$

by Jencks to quantify transition-state structure changes in carbonyl addition reactions.[22] Here there are six coefficients to be defined, but the chemical data usually yield only three known quantities relative to a fourth, namely, the energy of starting material. Therefore, coef-

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(19) (a) R. W. Alder (private communication) and later Wiberg[19b] have questioned whether chair 1,4-cyclohexanediyl is involved in the geometric isomerization of bicyclo[2.2.0]hexane as assumed in ref 7. Regardless of whether or not this is true, any reasonable estimate of $\Delta G_f{}^{523}$ of this diyl is at least 9 kcal/mol above that of the transition state for the [3,3] shift.[19c] (b) Wiberg, K. B.; Matturro, M. G. *Tetrahedron Lett.* **1981**, *22*, 3481. (c) Doering, W. von E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279.

(20) Equation 4 is an activation free energy response surface (AFERS) in three variables. For thermoneutral reactions, the AFERS is approximately a half section of a cone whose height relative to the plane is proportional to p. Inclusion of ΔG_r raises or lowers a particular point with respect to this surface.

(21) The AFERS (see footnote 20) for a thermoneutral nonconcerted reaction must resemble two contiguous sides of a square-base pyramid. It is possible to add a term in $\Delta G_x{}^{\ddagger} - \Delta G_y{}^{\ddagger}$ to eq 4 which will vary the shape of the AFERS to take into account this behavior.[7a]

(22) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948.

ficients a and b are arbitrarily set equal to one another so that eq 5 can be simplified to eq 6 where "a" is the adjustable parameter. Solving eq 6 for the values at the four corners ($x,y = 0$ or 1; $x = 1, y = 0$; $x = 0, y = 1$) yields eq 7, where there is only one parameter remaining which can be adjusted for each reaction type. Differentiation of eq 7 and setting the partial derivatives equal to zero allow a determination of the saddle point ($x^\ddagger$ and $y^\ddagger$). Substitution of these values into eq 6 gives eq 8 for the free energy of the saddle point. For the case where $\Delta G_r = 0$, eq 8 simplifies to eq 9. The similarity of eq 9 and 4 is clear.

$$\Delta G = a(x^2 + y^2) + cxy + dx + ey + f \qquad (6)$$

$$\Delta G = a(x^2 + y^2) + (\Delta G_r - \Delta G^\ddagger{}_x - \Delta G^\ddagger{}_y)xy + (\Delta G^\ddagger{}_x - a)x + (\Delta G^\ddagger{}_y - a)y \qquad (7)$$

$$\Delta G^\ddagger = \frac{cde - a(d^2 + e^2)}{4a^2 - c^2} \qquad (8)$$

$$c = \Delta G_r - \Delta G^\ddagger{}_x - \Delta G^\ddagger{}_y;\ d = \Delta G^\ddagger{}_x - a;\ e = \Delta G^\ddagger{}_y - a$$

$$\Delta G^\ddagger = \frac{\Delta G^\ddagger{}_x \Delta G^\ddagger{}_y - a^2}{\Delta G^\ddagger{}_x + \Delta G^\ddagger{}_y + 2a} \qquad (9)$$

Substituting the values for $\Delta G^\ddagger{}_x$, $\Delta G^\ddagger{}_y$, and ΔG_r into eq 8 gives a good correlation with $\Delta G^\ddagger{}_{xp}$ when $a = -27$ kcal/mol for the chairlike [3,3] shift (Table I). Interestingly, the results from eq 9 and 4 are similar in thermoneutral and exergonic reactions. The physical significance of a in eq 8 and 9 is that it is a measure of the degree of concert in the 1,5-hexadiene [3,3]-shift transition state. Thus, for the [3,3] shift of a 1,5-hexadiene with equivalent energy nonconcerted alternatives so that $x^\ddagger = y^\ddagger = {}^1/_2$, $\Delta G_{\text{concert}} = \min(\Delta G^\ddagger{}_{BB}, \Delta G^\ddagger{}_{BM}) - \Delta G^\ddagger{}_{xp} = {}^1/_2(\min(\Delta G^\ddagger{}_{BB}, \Delta G^\ddagger{}_{BM}) + a)$. For the parent structure where $\Delta G^\ddagger{}_x \simeq \Delta G^\ddagger{}_y \simeq 55$ kcal/mol, $\Delta G_{\text{concert}} = 14$ kcal/mol. Note that for a symmetrical transition state with lower nonconcerted ΔG's, the measure of concert is less.

The denominator of eq 8 makes it clear that a discontinuity occurs when ${}^1/_2|(\Delta G_r - \Delta G^\ddagger{}_x - \Delta G^\ddagger{}_y)| = |a|$. However, this discontinuity can occur only when both nonconcerted alternatives are very low in energy, a condition not normally encountered in the [3,3] shift. Importantly, eq 8 satisfies the microscopic reversibility criterion.

Parameters for $\Delta G^\ddagger{}_x$, $\Delta G^\ddagger{}_y$, and ΔG_r. To obtain the parameters for application of eq 4 or 8, it is necessary to determine the effect of substituents on the known $\Delta G^\ddagger$ for cleavage of 1,5-hexadiene (57 kcal/mol at 250 °C), on the reasonably estimated value for formation of cyclohexane-1,4-diyl (53 kcal/mol at 250 °C), and on ΔG_r.

Radical-stabilizing groups on C-3 and C-4 will lower $\Delta G^\ddagger{}_y$ (bond fission) by their radical-stabilization energies (RSE). Substituents in C-2 and C-5 will lower $\Delta G^\ddagger{}_x$ (bond formation) by the RSE but will often stabilize the ground state by conjugative interactions (CI). The CI values also allow determination of ΔG_r. Table II lists representative values for RSE's and CI's that are generally agreed upon in the literature. In particular, CI values can be taken from Hine's work, and they agree with those determined by heats of hydrogenation. The latest listing of BDE's which allows a determination of RSE's has been provided by McMillen and Golden. However, there is controversy over the BDE of simple C–C single bonds (see Doering[19c] for a review), and it appears that most RSE's have roughly a ±5% uncertainity. Further, the uncertainity in the RSE's of α-carbonyl and α-cyano far exceed this limit. For instance, from pyrolysis of acetylcyclobutane a RSE for α-carbonyl of 8 kcal/mol can be estimated, yet the McMillen and Golden listing of BDE's allows a calculation of only 3 kcal/mol for this RSE. More disconcerting is the RSE of α-cyano. Extensive work by King and Goddard have led them to 8 kcal/mol as the α-cyano RSE; yet their kinetics on the pyrolysis of propyl cyanide ($\log k/s = 15.4$ $(76.6 \pm 1.7$ kcal/mol$)/\theta$)[23] leads to a value of 13 kcal/mol when the $\Delta H^\ddagger$ is compared to the strengths of the C–C bond in propane according to the upwardly revised C–C BDE'sby Doering.[19c]. The RSE of α-carboalkoxy is not well documented, although by examination of cyclobutane and cyclopropane pyrolyses it may be 6–8 kcal/mol.

Table II

substituent	RSE[a] ($\Delta\Delta H_f$'s rel to H), kcal/mol	CI (from Hine),[d] kcal/mol
allyl	2.5	2.5
Br	~2.5	7.7
Cl	~2.5	2
OR	2.5	4.9
$CH{=}CH_2$	12.5[b]	6
CN	13[e]	3.5
CO_2R	7	3.6
Ph[b]	14[b]	4.5
$CH{=}CHCH{=}CH_2$[c]	19	~10

[a] McMillen, D. I.; Golden, G. M. *Annu. Rev. Phys. Chem.* **1982**, *37*, 493. [b] Reference 10. [c] Alonso, J. H.; Dolbier, W. R., Jr.; Frey, H. M. *Int. J. Chem. Kinet.* **1974**, *6*, 893. [d] Hine, J.; Skoglund, M. J. *J. Org. Chem.* **1982**, *47*, 4766. [e] See discussion.

Using the values in Table II, it is possible to calculate $\Delta G^\ddagger{}_x$, $\Delta G^\ddagger{}_y$, and ΔG_r for typical [3,3] shifts: e.g., $\Delta G^\ddagger{}_x$ for the [3,3] shift of 2-phenyl-1,5-hexadiene is 53 − 15(RSE) + 5(CI) = 43 and $\Delta G^\ddagger{}_x = 57$ kcal/mol at 250 °C, assuming that the ground-state stabilization by phenyl is also present in the radical site. This point has not been adequately tested in bona fide radical processes, but in the barbaralane [3,3] shift where the transition state probably resembles two ally radicals, phenyl substitution at positions equivalent to C-2 and C-5 made little change in $\Delta G^\ddagger$.[24]

An important point in connection with RSE's is the effect of groups on radical sites already stabilized by a vinyl, phenyl, or cyano group; it appears that the RSE is about two-thirds the value that it is when attached to an unstabilized radical. For instance, the pentadienyl radical stabilization energy is 19 kcal/mol, which is roughly 1.6 times the allyl radical resonance energy (see Table II). Thus, substitution of a phenyl on C-3 (or on C-1) of 1,5-hexadiene will affect $\Delta G^\ddagger{}_y$ (bond breaking) not by 15 kcal/mol but by about 10 kcal/mol. Finally, strain energies in ground states and in nonconcerted alternatives must be considered, and a good source of these data is the Liebman and Greenberg review.[25]

Evaluation and Further Applications

General Remarks. Given the assumptions of the models, their reproduction of the data of Table I is remarkable. However, there is still the problem indicated previously and amplified below that the models do not reduce to single edge potentials when one nonconcerted alternative is much more stable than the other. Thus extreme substitution on a concerted reaction that forces a stepwise process may not be well-handled by the models although none of the known systems behaves badly except as noted below. Indeed, the models give a larger $\Delta G^\ddagger$ than

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(23) King, K. D.; Goddard, R. D. *Int. J. Chem. Kinet.* **1975**, *7*, 837.
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Table III. Boatlike [3.3] Shifts^{m} at 523 K

compd	$\Delta G^{\ddagger}{}_{y}$BB (bond breaking)	$\Delta G^{\ddagger}{}_{y}$BM (bond making)	ΔG_{r}	$\Delta G^{\ddagger}{}_{xp}{}^{a}$	$\Delta G^{\ddagger}{}_{calcd}$ eq 4, $p = 1.5$	eq 8
1,5-hexadiene (boat)	57	63	0	47	45	44
1,4-dimethylenecyclohexane	57	66^{b}	0	47	46	44
cis-1,2-divinylcyclobutane	35^{c}	60^{d}	−14^{e}	28	29	32
bicyclo[6.2.0]deca-2,6-diene	35^{f}	70	0	35	35	34
cis-1,2-divinylcyclopropane	33.5^{g}	60^{d}	−20^{h}	22	26.8	34
3,4-homotropilidene	33.5^{f,g}	72^{i}	0	12	34*	
bicyclo[6.1.0]nona-2,6-diene	33.5^{f,g}	71^{j}	−7	24.5	32	
semibullvalene	16^{k}	72^{i}	0	7.4	20*	
bullvalene	25^{l}	72^{i}	0	14	28*	9

[a] Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981. [b] 53 + 12 kcal/mol (12 kcal/mol is the strain energy of bicyclo[2.2.2]octane). [c] The $\Delta G^{\ddagger}$ for reaction of *trans*-1,2-divinylcyclobutane; see footnote *a*. [d] 63 − 3 kcal/mol ($T\Delta S$ correction for one frozen rotation in the ground state). [e] 26 − 12 kcal/mol (the strain energy in cyclobutane minus the SE of a *c*,*c*-C_8 diene). [f] Assumes that the SE in starting material is the same as the SE in the diradical excluding the small ring. [g] The $\Delta G^{\ddagger}$ for reaction of *trans*-1,2-divinylcyclopropane; see footnote *a*. [h] The SE of 1,4-cycloheptadiene is 7 kcal/mol. [i] 53 + 27 (SE in cyclopropane) − 8 ($T\Delta S$ for three frozen rotations) kcal/mol. [j] 53 + 26 (SE in cyclobutane) − 8 ($T\Delta S$ for three frozen rotations) kcal/mol. [k] 57 − 44 [ring strain (calculated by MNDO: J. J. Dannenberg, private communication)] + 3 (an entropy correction due to no "free fragments" in the transition state) kcal/mol. [l] 57 − 35 [SE of bullvalene Mansson, M.; Sunner, S. *J. Chem. Thermodyn.* 1981, *13*, 671)] + 3 (an entropy correction) kcal/mol. [m] All *G* values are given in kilocalories per mole.

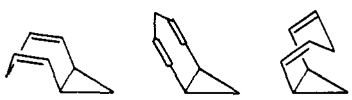
the $\Delta G^{\ddagger}$ of a highly favored nonconcerted alternative. Nevertheless, the models provide an insight into a prediction of substituent effects on concerted reactions within the limits of accuracy of RSE's. Further, the models suggest that ΔG_r affects the transition state only to a small extent. Typically, increasing the reaction exergonicity lowers the calculated $\Delta G^{\ddagger}$ by an additive term equal to roughly one-quarter the amount of the increase. This change is roughly independent of the magnitude of $\Delta G^{\ddagger}$. This is not unlike Marcus theory predictions for two-dimensional energy surfaces where the calculated $\Delta G^{\ddagger}$ changes by an additive term equal to roughly half the change in ΔG_r.[26] The magnitude of the additive term is also roughly independent of $\Delta G^{\ddagger}$ so long as $\Delta G^{\ddagger}$ is not near zero.

Boatlike [3,3] Shifts. Boatlike [3,3] shifts have very different transition-state geometries and electronic structures compared to chairlike transition states and so a separate analysis is necessary. In particular, the $\Delta G^{\ddagger}$ for bond making (to give a boat 1,4-cyclohexanediyl) might be expected to be higher than that for the comparable chair arrangement. For the calculations below, it is assumed that the transition-state energy of the boat diyl is 10 kcal/mol higher than that of the chair. This estimate relies on the known $\Delta G^{\ddagger}$ for chair–chair cyclohexane interconversion with the assumption that the repulsion in the antisymmetric diyl compensates for the loss of 1,4-hydrogen interaction. The $\Delta G^{\ddagger}$ for bond breaking, particularly of bonds in medium rings as in homotropilidene, will be affected by strain energies, and these are estimated in the usual way with comments on individual cases.

Listed in Table III are the experimental and calculated values of $\Delta G^{\ddagger}$ at 523 K for a number of boatlike [3,3] shifts. Included are the bicyclic systems such as bullvalene and semibullvalene when the strain energies have been either determined or calculated.

Remarkably, the correlations for all but the *cis*-1,2-divinylcyclopropane (DVΔ) rearrangements are best with the same *p* or nearly the same *a* as used for the chairlike reactions. However, the calculated values for the DVΔ-type reactions are invariably too high. Analysis of many of these (starred entries of Table III) reveals that the calculated $\Delta G^{\ddagger}$ is somewhat higher than that for the pure bond breaking process, $\Delta G^{\ddagger}{}_{y}$. Clearly, the inadequacies of the correlation equations described above become obvious in these reactions where the transition state appears to closely resemble two allyl radicals. That the transition state should resemble the allyl radicals comes from unpublished work of José Jimenez, who found that the inverse KIE at the terminal carbons in the [3,3] shift of *cis*-1,2-divinylcyclobutane is only $^{1}/_{20}$ of the equilibrium isotope effect, suggesting little interaction between the terminal carbons in this transition state. It would be remarkable if the cyclopropane cases would be dramatically different; the KIE's are currently being determined to check this point. It should also be noted that radical-stabilizing groups on C-2 and C-6 of semibullvalenes cause a rate increase[27] while these same groups at C-3 and C-7 retard the rate of the semibullvalene rearrangement.[28] This is consistent with a two-allyl radical-like transition state.

Chart I



	extended	planar	saddle
MNDO $\Delta H_f{}^{298}$, kcal/mol	39.0	40.8	40.6
group additivity $\Delta H_f{}^{298}$, kcal/mol	53		

The most glaring discrepancy between the experimental value and $\Delta G^{\ddagger}$ for bond breaking is that of homotropilidene (22 kcal/mol!). The calculation for pure bond breaking assumes that there is little energy difference between the extended and saddle conformations (Günther estimated that the saddle conformation is 2 kcal/mol higher than the extended form)[29] and that the strain in the diradical is the same as the strain in the seven-membering ring of the starting material (see Chart I). The estimate for bond making assumes no conjugation between

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(26) For a discussion of this behavior in proton-transfer reactions, see: Murdoch, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 4410.

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Table IV. Aliphatic Claisen Rearrangements at 523 K[a]

compd	$\Delta G^{\ddagger}_x$ (bond making)	$\Delta G^{\ddagger}_y$ (bond breaking)	ΔG_r	$\Delta G^{\ddagger}_{xp}$ at 523 K[11]	$\Delta G^{\ddagger}_{calcd}$ eq 4, $p = 1.5$	$\Delta G^{\ddagger}_{calcd}$ eq 8, $a = -23$
allyl vinyl ether	57	47	−17	33.6	33.2	33.3
1-cyano	60.5 (57 + 3.5)	41.5 (47 − 9 + 3.5)	−13.5 (−17.0 + 3.5)	33.1	32.6	32.6
2-cyano	47.5 (57 − 13 + 3.5)	47	−17	29.7	30.0	31.3
4-cyano	57	38 (47 − 9)	−20.5 (−17 − 3.5)	29.8	28.1	29.5
5-cyano	47.5	47	−17	31.8	30.0	31.3
6-cyano	60.5 (57 + 3.5)	41.5 (57 + 3.5)	−13.5 (−17 + 3.5)	34.6	32.6	32.6

[a] All *G* values are given in kilocalories per mole.

the radical sites and the two cyclopropane rings as is the case with bullvalene and semibullvalene. Of further concern is the revelation from molecular models of the saddle geometry necessary for the [3,3] shift in homotropilidene of the presence of a severe nonbonded H–H repulsion not present in the extended conformation. Thus, it is even more surprising that the [3,3] shift of homotropilidene is as rapid as is observed. For assessment of the relative energies of the extended and saddle conformation, MNDO calculations were performed with complete geometry optimization by assuming no symmetry, and, surprisingly, only a 1.6 kcal/mol difference in energy was found. Moreover, the absolute ΔH_f of the extended form was 14 kcal/mol lower than the group additivity[10] estimated ΔH_f, assuming the strain energy is the sum of a cyclopropane and of tropilidene (the correction for tropilidene is 4.7 kcal/mol, which is nearly the same for all seven-membered rings with and without double bonds).[10] Further, both saddle and extended geometries were calculated to have flattened seven-membered rings, and even the enforced planar geometry (all H—C═C—H torsion angles fixed at 0° and all C—C—C—C torsions in the seven-membered ring set equal to 0°), which might be expected to be a transition state between the two stable conformations, was only 0.2 kcal/mol above the saddle. In view of the 9-kcal/mol underestimate of ΔH_f for tropilidene itself, giving a near-planar structure, it is clear that MNDO overestimates electron delocalization in these systems. It must be concluded that no understanding of the facility [3,3] shift of homotropilidene is provided by the current frame of reference nor by any other, although it does represent an extreme behavior foreshadowed by the reaction of *cis*-1,2-divinylcyclopropane itself and derivatives like bicyclo[6.1.0]nona-2,6-diene. These boatlike reactions of *cis*-1,2-divinylcyclopropane can be better correlated with eq 4 if p were equal to 1 or with eq 8 if $a = 0$, all of which implies that there is extra stabilization of the transition state relative to other chair and boatlike [3,3] shifts. The origin of this stabilization is unclear.

C-1-Substituted 1,5-Dienes. There are few systematic studies of substituents at C-1 of 1,5-hexadienes, but in unpublished work J. Emrani has found that the $\Delta G^{\ddagger}$'s for degenerate [3,3] shifts of 1,3- and 1,4-diphenyl-1,5-hexadiene are very similar to that of 3-phenyl-1,5-hexadiene. This suggests that C-1 substitution here stabilizes the ground state and increases both $\Delta G^{\ddagger}_x$ (bond making) and $\Delta G^{\ddagger}_y$ (bond breaking).

Thus for 1,4-diphenyl-1,5-hexadiene, $\Delta G^{\ddagger}_x$ (BM) = 53 + 5 (CI of 1-phenyl) = 58 kcal/mol, and $\Delta G^{\ddagger}_y$ (BB) = 57 − 10(RSE of 4-phenyl) −5 (RSE of C-1 phenyl − CI of 1-phenyl) = 42 kcal/mol. By use of eq 4 with $p = 1.5$, the calculated $\Delta G^{\ddagger}$ is 36.3 kcal/mol which is within 1 kcal/mol of the experimental value. A similar calculation applies to 1,3-diphenyl-1,5-hexadiene.

Claisen Rearrangements. Carpenter has found that substitution of a cyano group at either terminus of allyl vinyl ether has no accelerating effect on the [3,3] shift; in fact, substitution at C-6 retards the rate by a factor of 9.[11] Further, the efficiency of eq 4 in dealing with all the experimental results has been called into question. In addition, Carpenter found that his model could rationalize the direction of the rate responses of the Claisen rearrangement to substitution of a cyano group of all five carbon positions. Table IV lists the experimental and calculated $\Delta G^{\ddagger}$ for Carpenter's systems at 523 K along with the values of $\Delta G^{\ddagger}_x$ and $\Delta G^{\ddagger}_y$ used. There is, in fact, a fair quantitative correlation between the calculated and experimental values with $p = 1.5$ on using eq 4 and particularly when it is recognized that most of the calculated values are a little low, suggesting that the parameters for the parent compound are a little low. This is because the $\Delta G^{\ddagger}_x$, $\Delta G^{\ddagger}_y$, and ΔG_r for all the cyano-substituted materials used the parameters for the parent as a base. The resonance energy of α-cyano was taken as 13 kcal/mol except when it is attached to an already stabilized radical as in the 1-, 4-, or 6-cyano-substituted material where its RSE was assumed to be 9 kcal/mol (the two-thirds factor; see the parameters section). The CI of cyano is ~3.5 kcal/mol which affects $\Delta G^{\ddagger}_x$, $\Delta G^{\ddagger}_y$, and ΔG_r, depending on the substitution. The correlation of Carpenter's data is not superb, but when it is considered that the ground-state and nonconcerted alternatives may have some charge polarization which can be altered by cyano at various positions, the correlation is surprisingly good.

A final reaction of concern is the facile [3,3] shift of ketene allyl silyl acetals ($\Delta G^{\ddagger} \simeq 24$ kcal/mol).[30] The correlation equations predict a $\Delta G^{\ddagger}$ of 26 kcal/mol on assuming that the siloxy group is equivalent to methoxy in affecting $\Delta G^{\ddagger}_y$ and $\Delta G^{\ddagger}_x$; the prediction results from a 12 kcal/mol stabilization of the bond breaking alternative. Unpublished work by J. Emrani using secondary deuterium isotope effects and phenyl substituent effects suggests that the transition state resembles two allylic species, indicating that $\Delta G^{\ddagger}_y$ (bond breaking) is substantially lowered by siloxy substitution at C-2. This is a remarkable effect of oxygen to promote a dissociative 2-allyl-like transition state.

Thus, it would appear that reactions which deviate from the correlation equations involve stabilization effects out of the ordinary realm of group contributions and simple radical stabilization energies. These deviant systems therefore should be objects of further mechanistic and theoretical scrutiny. Of course, the calculations depend on radical stabilization energies which themselves are not without controversy.

Acknowledgment. We thank the National Science Foundation for generous financial support and the Weizmann Institute of Science for a Fellowship to K.E.G.

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J. Org. Chem. **1984**, *49*, 17-20

Registry No. 1,5-Hexadiene, 592-42-7; 2-phenyl-1,5-hexadiene, 7399-52-2; 3-phenyl-1,5-hexadiene, 1076-66-0; 2,5-diphenyl-1,5-hexadiene, 7283-49-0; 2,5-dicyano-3-methyl-1,5-hexadiene, 63472-80-0; *threo*-3,4-dimethyl-1,5-hexadiene, 68701-55-3; *threo*-3,4-diphenyl-1,5-hexadiene, 80754-12-7; 2,4-diphenyl-1,5-hexadiene, 63779-63-5; allyl vinyl ether, 3917-15-5; allyl phenyl ether, 1746-13-0; allyl acetate, 591-87-7; 1,4-dimethylenecyclohexane, 4982-20-1; *cis*-1,2-dimethylcyclobutane, 16177-46-1; bicyclo[6.2.0]deca-2,6-diene, 77614-69-8; *cis*-1,2-divinylcyclopropane, 2984-58-9; 3,4-homotropilidene, 3725-20-0; bicyclo[6.1.0]nona-2,6-diene, 30767-77-2; semibullvalene, 6909-37-1; bullvalene, 1005-51-2.

Reactivities of Cycloalkenes toward Phenylthio Radicals

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The absolute rate constants for the addition reactions of the (*p*-chlorophenyl)thio radical toward cyclomonoalkenes, cycloalkadienes, and bicycloalkenes have been determined by the flash photolysis method by taking the reversibility of the addition process into consideration. The reactivities toward $p\text{-ClC}_6\text{H}_4\text{S}\cdot$ are proportional to those toward the methyl radical. The rate constants (in $M^{-1}\ s^{-1}$) decrease in the order conjugated dienes (10^6–10^8) > bicycloalkenes (10^5–10^7) > cyclomonoalkenes (10^2–10^5). The reactivities are controlled by the resonance stabilization of the transition state, by the released strain energy, and by the polar nature of the transition state.

Introduction

The relative reactivities of cycloalkenes in free-radical addition reactions have been reported for the carbon-centered radicals,[1-3] the bromine atom,[4] and the thio radicals.[5-8] The reactivities, however, vary with the kinds of the attacking radicals. One of the origins of the difference in the reactivities is attributed to the reversibility of the addition step for radicals; in the case of the thio radicals reliable data have not been obtained since the reactivity ratios depend upon the concentrations of the chain-transfer reagents.[7] Therefore, a new kinetic approach that explicitly includes the reversibility of the addition step is required. We found that the flash photolysis method is useful to obtain the absolute rate constants for the reversible addition reactions of the phenylthio radicals with alkenes[9] and alkynes;[10] the difficulty of the reversibility can be overcome by addition of a selective radical trap that is not reactive to the thio radicals but reactive to the adduct carbon-centered radicals. In this study we have applied this method to cycloalkenes and examined the factors controlling the reactivities.

Results

The flash photolysis method of determining the rates of addition of the phenylthio radicals has been described in a previous paper;[9a] the procedure is briefly shown below.

Scheme I

$$\text{PhSSPh} \underset{k_r}{\overset{h\nu}{\rightleftharpoons}} 2\text{PhS}\cdot \qquad (1)$$

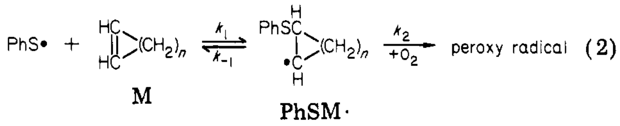

Table I. Addition Rate Constants (k_1) and Relative Equilibrium Constants (Kk_2) for Reactions of $p\text{-ClC}_6\text{H}_4\text{S}\cdot$ toward Cyclomonoalkenes at 23 °C[a]

alkenes	k_1, $M^{-1}\ s^{-1}$	Kk_2, $M^{-2}\ s^{-1}$
cyclopentene[c]	4.2×10^4	2.7×10^6
cyclohexene[b]	3.3×10^3	2.0×10^5
cycloheptene[c]	1.1×10^5	8.2×10^6
cyclooctene[b]	2.5×10^3	1.9×10^5
cyclododecene[c]	8.2×10^2	8.3×10^4

[a] Each estimation error is ca. 10%. [b] In each alkene. [c] In cyclohexane.

In this study, the (*p*-chlorophenyl)thio radical was selected as a representative of the phenylthio radicals because the sharp transient absorption band yields precise data. The transient absorption band at 515 nm generated by the flash photodecomposition of bis(*p*-chlorophenyl) disulfide was ascribed to $p\text{-ClC}_6\text{H}_4\text{S}\cdot$ since the same absorption band was observed by the flash photolysis of the corresponding thiol.[11] The initial concentration of the thio radical generated by one flash exposure is estimated to be ca. 10^{-6} M by assuming the diffusion-controlled rate constant for recombination of the thio radical.[9] Low reactivity of the phenylthio radical toward oxygen was confirmed since the decay rate of the phenylthio radical was not accelerated by the addition of oxygen into solution. The low hydrogen-abstraction ability of the phenylthio radical was also confirmed.[9a]

Figure 1 shows the first-order plots of the decay curves of $p\text{-ClC}_6\text{H}_4\text{S}\cdot$ in cyclohexane. Curve b is the plot in de-

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