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THE EFFECT OF TRANSITION STATE BOND ORDER ON SIGMATROPIC SHIFTS AND CYCLOADDITION REACTIONS

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Abstract - A recently developed classical model for the calculation of activation free energies of chemical reactions is applied to the study of sigmatropic shifts and cycloaddition reactions. The model does not require the consideration of parallel or perpendicular effects along the reaction coordinate to interpret substituent effects. These reactions can be treated as any other ordinary chemical reation, and the effect of substituents is explained in terms of an increase in the bond order of the transition state, $n^{\ddagger}$, due to an increase in the electronic charge produced by the substituents on the carbon skeleton. Secondary isotope effects are also explained in terms of $n^{\ddagger}$. The model estimates absolute $\Delta G^{\ddagger}$ for the main reactions in good agreement with experiment, under the assumption that the processes are concerted and synchronous and consequently $n^{\ddagger} = 0.5$. The nonlinear character of the free energy relationships for these reactions is attributed to the variation of $n^{\ddagger}$ upon substitution. Some of the apparent violations of the Woodward-Hoffmann rules on the conservation of orbital symmetry in concerted reactions can be treated in a similar way. The synchronism of these reactions is also discussed.

Sigmatropic shift reactions have been extensively studied in order to assess their concerted nature [1] and to interpret substituent effects which cannot be studied in terms of linear free energy relationships.[2,3] Theoretical models based on transverse effects of structures along the reaction coordinate have been employed to quantitatively interpret substituent effects on the shift and on cycloaddition reactions.[4] These two dimensional potential energy surfaces have been questioned on the grounds that they do not interpret kinetic isotope effects and bear no resemblance to potential energy surfaces current in molecular dynamics.[5] Agmon has proposed an alternative model based on one-dimensional reaction energy curves, where effects of structures perpendicular to the reaction coordinate can be described by an upside-down free energy profile.[5] However both models require parameters adjustable to kinetic data.

We have recently developed a model to estimate activation free energies for reactions in the vapour phase and in solution,[6] which has been found to be more general than BEBO[7] and Marcus[8] theories, and which for thermoneutral reactions is based on empirical relations outside the field of kinetics. We therefore feel it useful to apply such a model to the study of sigmatropic shift and cycloaddition reactions, not only to interpret substituent and isotope effects, but also to interpret the absolute value of $\Delta G^{\ddagger}$ for the main reactions, in terms of molecular and thermodynamic parameters. We will also show that these reactions can be treated as any other ordinary chemical reaction, as long as the role of the bond order at the transition state is properly assessed.

Theoretical Model

Most organic reactions are one-bond process, involving either the making and breaking of one bond or distinct steps where a simple bond is formed or broken.[9] Let us assume for simplicity that the potential energy curves of these reactive bonds can be represented by harmonic oscillators with a common force constant f. The activation free energy for the reaction given by the intersection of two paraboles separated by a distance d, is

$$\Delta G^{\ddagger}=(\Delta G^{o}+(1/2)fd^{2})^{2}/2fd^{2} \qquad (1)$$

where ΔG^{o} is the reaction free energy and d represents also the sum of the bond distensions of reactant and product to the transition state. We have shown [6] that d is proportional to the sum of the equilibrium lengths of the reactive bonds,

$$d = \eta\,(l_r + l_p) \qquad (2)$$

where η is a reduced bond distension, [6b]

$$\eta = \frac{a' \ln 2}{n^{\ddagger}} + \frac{a'}{2\lambda^{2}}(\Delta G^{o})^{2} \qquad (3)$$

a' is an universal constant (a' = 0.156) and $n^{\ddagger}$ is the average bond order of the reactive bonds at the transition state. The configuration entropy parameter, λ, proposed by Agmon and Levine [10] is only a significant parameter to estimate $\Delta G^{\ddagger}$ for reasonably high endothermic or exothermic reactions. Consequently, when ΔG^{o} is close to zero or $\lambda >> |\Delta G^{o}|$, the activation free energy can be estimated from the knowledge of the force constant, f, the equilibrium bond lengths l_r and l_p, the reaction free energy ΔG^{o} and the bond order at the transition state $n^{\ddagger}$. The parameters f, l_r, l_p and ΔG^{o} can be known from spectroscopic and thermodynamic data. The bond order $n^{\ddagger}$ depends on the nature of the reaction.

For one-bond reactions, involving single bonds (n=1), the conservation of the total bond order, [7] $n_p + n_r = 1$, requires that at the transition state the average bond order is $n^{\ddagger} = 1/2$. However, this is only valid for a synchronous and concerted reaction.[§] If the reaction is concerted, but is not synchronous then $n^{\ddagger} < 1/2$. We have also shown[6] that for some reactions the total bond order can increase if antibonding or nonbonding electrons acquire a bonding character at the transition state. Then $n_p + n_r = m\ (m>1)$ and for a synchronous reaction $n^{\ddagger} = m/2$, whereas for a nonsynchronous process $n^{\ddagger} < m/2$; m is the maximum possible bond order value which can be known from simple molecular orbital theory.[11].

Dewar [9] has suggested that synchronous multibond reactions are normally prohibited, with some exceptions where there are some special advantages of synchronicity. Sigmatropic rearrangements and cycloadditions are currently considered as synchronous and concerted processes, but Dewar has raised some doubts about such ideas. Consequently the analysis of such reactions within the general intersecting-state model may contribute to a clarification of this problem. Although the present model has been developed for collinear atom+diatom reactions, it can be extended to multibond processes if a judicious choice of the effective force constant along the reaction coordinate is made.

Sigmatropic Reactions

The 3,3-shifts of 1,5-hexadienes is a convenient reaction to study theoretically

because all the necessary kinetic and thermodynamic data are known.[1-3] The relevant molecular parameters can also be easily estimated if the reaction is represented in terms of the transformation of only one chemical bond. The stretching force constant can be considered as an average of $2f_{C=C}$ and $3f_{C-C}$ distributed between six effective bonds in the bond-breaking bond-forming processes. With $f_{C=C}=5.8\times10^{3}$ kJ mol^{-1}A^{o-2} and $f_{C-C}=2.7\times10^{3}$ kJ mol^{-1} A^{o-2},[12] then $f=3.3\times10^{3}$ kJ mol^{-1}A^{o-2}. This value is, in fact, close to the carbon-carbon stretching force constant in benzene, $f=3.1-3.4\times10^{3}$ kJ mol^{-1} A^{o-2}. The average equilibrium bond length in the reactant or the product is $(2\,l_{C=C}+3\,l_{C-C})/5$ which with $l_{C=C}=1.335$ A^{o} and $l_{C-C}=1.537$ A^{o} [12] leads to $l_r+l_p=2.912$ A^{o}.

[§] A synchronous reaction is one where all the bond-making and bond-breaking processes take place in unison. A concerted reaction is one that takes place in a single kinetic step, without necessarily being synchronous.

The sigmatropic shift reaction under study involves the breaking and forming of several chemical bonds, but all the processes ($n=1 \rightleftarrows n=2$, $n=1 \rightleftarrows n=0$) are equivalent to bond-breaking bond-forming processes of single chemical bonds. Consequently, if this reaction is a synchronous process $n^{\ddagger}=1/2$. Since $\Delta G^{o}=0$ we have all the necessary data to estimate $\Delta G^{\ddagger}$ and compare the calculated and the experimental ($\Delta G^{\ddagger}=171$ kJ mol^{-1}) values.[2] With $f=3.3\times10^{3}$ kJ mol^{-1} A^{o-2} the calculated is $\Delta G^{\ddagger}=163$ kJ mol^{-1} and with $f=3.4\times10^{3}$ kJ mol^{-1} A^{o-2} $\Delta G^{\ddagger}=168$ kJ mol^{-1}. The calculated values agree with the experimental value with an error <5%. This supports the view[1] that this sigmatropic shift reaction is essentially synchronous, otherwise $n^{\ddagger}<1/2$ and the calculated activation free energy would be much higher than the experimental value. The present findings also support the use of harmonic stretching oscillators for the potential energy curves. This assumption is convenient because $\Delta G^{\ddagger}$ is much lower than the dissociation energies of the carbon-carbon bonds in hexadienes. Furthermore any contribution from bending or twisting modes which are not associated with the bond stretches cannot be very significant.[§]

Although the present calculation supports the concerted character of the sigmatropic rearrangement of 1,5-hexadiene we can also consider the possibility of a nonconcerted reaction involving the biradical intermediate 1,4-cyclohexylene. Now the bond-forming bond-breaking process involve only the following chemical bonds 1-2, 5-6 and 1-6, and consequently $f_r=(2/3)f_{C=C}=3.9\times10^{3}$ kJ mol^{-1}, $f_p=f_{C-C}$ and $l=l_{C=C}+l_{C-C}=2.872$ A^{o}. With this set of values and $\Delta G^{o}=146$ kJ mol^{-1} [13], $\Delta G^{\ddagger}=243$ kJ mol^{-1} with $n^{\ddagger}=1/2$. Assuming the more likely situation [6] that the two unpaired electrons can acquire a bonding character at the transition state, then this contribution over 6 bonds leads to $n^{\ddagger}=0.667$ and $\Delta G^{\ddagger}=181$ kJ mol^{-1} which is almost 20 kJ mol^{-1} higher than the corresponding value calculated for the concerted reaction. The same situation has also been found by Gajewski [1,3] who estimate $\Delta G^{\ddagger}\simeq220$ kJ mol^{-1} for this nonconcerted pathway.

To interpret the substituent effects in these reactions it is more convenient to adjust f in order to reproduce the activation free energy in 1,5-hexadiene ($n^{\ddagger}=1/2$) and with this adjusted value ($f=3.465\times10^{3}$ kJ mol^{-1}A^{o-2}) calculate the bond distensions parameter d which reproduce $\Delta G^{\ddagger}$ for the other reactions. Table 1 presents the results of such a calculation, together with the reduced bond distension, η. The bond order of the transition state, $n^{\ddagger}$, is then calculated through eq (3) when $\lambda \gg |\Delta G^{o}|$, i.e., $n^{\ddagger}=0.108/\eta$. For the allyl vinyl ether the appropriate corrections due to the presence of a C-O bond ($f_{C-O}=3\times10^{3}$ kJ mol^{-1} A^{o-2}, $l_{C-O}=1.426$ A^{o})[12] were introduced in the calculation.

For some of the compounds $n^{\ddagger}=0.5$ as in 1,5-hexadiene. For such cases the effect of substituents is simply an effect on ΔG^{o}. However, for many other compounds $n^{\ddagger}>0.5$. For very exothermic reactions such as the ones of allyl vinyl ether and 3-oxyanion-1,5-hexadiene, this can be due to the effect of ΔG^{o} on η (eq(3)), but for the other cases $n^{\ddagger}>0.5$ means that there is a siphoning of electronic density from the substituent into the main hexadiene skeleton, at the transition state. Of the substituents considered in Table 1 only the phenyl and cyano groups, which possess π electrons, produce an increase in electronic charge in the carbon skeleton; methyl groups do not have such an effect. Although cyano group is usually considered to be an effective electron withdrawing substituent for ground state species, it is known that their π orbitals can have a back-donating effect.

Table 1. Bond Distensions and Transition State Bond Orders in 3,3-Sigmatropic Shifts

	$\Delta G^{\ddagger}$/kJ mol^{-1} [a]	ΔG^{o}/kJ mol^{-1} [a]	d/A^{o} [b]	η [b]	$n^{\ddagger}$	lnKIE/lnEIE
1,5-hexadiene	171.4	0	0.629	0.216	0.5	0.64
2-phenyl-1,5-hexadiene	148.4	0	0.585	0.201	0.538	0.75
2,5-diphenyl-1,5-hexadiene	129.6	0	0.547	0.188	0.575	0.87
3-phenyl-1,5-hexadiene	150 [d]	-9.5	0.598	0.205	0.526	
3,4-dimethyl-1,5-hexadiene	163.0	-18.8	0.631	0.217	0.50	
3,3-dicyano-1,5-hexadiene	133.8	-18.8	0.574	0.197	0.547	
3,4-diphenyl-1,5-hexadiene	129.6	-18.8	0.566	0.194	0.556	
allyl vinyl ether [c]	137.9	-71.1	0.620	0.216	0.50	
3-oxyanion-1,5-hexadiene	108.7	-79.4	0.58	0.199	0.542	

[a] Ref 2. [b] $f=3.465\times10^{3}$ kJ mol^{-1} A^{o-2}, $l_r+l_p=2.912$ A^{o}. [c] $f=3.57\times10^{3}$ kJ mol^{-1} A^{o-2}, $l_r+l_p=2.868$ A^{o}. [d] Ref 13. [e] Refs 3 and 5.

[§] There is some proportionality between stretching and bending force constants, which suggests that these motions are not completely independent.

Dewar[9,14] and coworkers have suggested that some of the rearrangements for substituted 1,5-hexadienes can be nonsynchronous processes. For synchronous reactions we would have expected that the position of the substituent does not alter $n^{\ddagger}$. This is not the case for the phenyl substituents; the substituents in the positions 2 and 5 produce an higher increase in $n^{\ddagger}$ than in positions 3 and 4. The maximum increase in $n^{\ddagger}$ per phenyl group can correspond to the siphoning of a pair of electrons into the carbon skeleton, i.e., $\Delta n^{\ddagger}=0.17$. Since such increase is not observed, these sigmatropic shifts can be concerted and nonsynchronous reactions.

The relative values of secondary α-deuterium isotope effects at the bond-making and bond-forming sites of 1,5-hexadienes vary as a function of substitution.[1,3] The kinetic isotope effect ratio KIE=BMKIE/BBKIE would be expected to be related to the extent of bond-breaking and bond-making. In a degenerate rearrangement KIE resulting from deuterium substitution on the bond-breaking sites (or bond-making sites) are related by an equilibrium isotope effect (EIE) which represents the KIE for complete change in bonding. These ratios (Table 1) could in principle be interpreted as measures of the degree of progress of the reaction in the respective transition state. Such a progress can be measure by x/d where x is the average bond distension from reactant to the transition state. However, for thermoneutral reactions x/d=0.5 and there is a significant variation in the ratio of the secondary isotopic effect.

Winey and Thornton,[15] and Agmon[5] have shown that the ratio of the isotope effects expressed by lnKIE/lnEIE is directly related to bond order changes, when reactions under identical conditions (e.g. $\Delta G^{o}=0$) are compared. We expect that such ratio should be proportional to $n^{\ddagger}$, because for a thermoneutral reaction $n^{\ddagger}$ represents the bond order change from reactant to the transition state. Figure 1 shows that a linear relationship is observed for the three reactions with $\Delta G^{o}=0$. The extrapolated bond order for lnKIE/lnEIE=1.0 is $n^{\ddagger}=0.62$. The addition of a pair of electrons for a complete bond forming process would lead to $n^{\ddagger}=0.67$. For a nonsynchronous process the complete change in bonding can correspond to $n^{\ddagger}<0.67$.

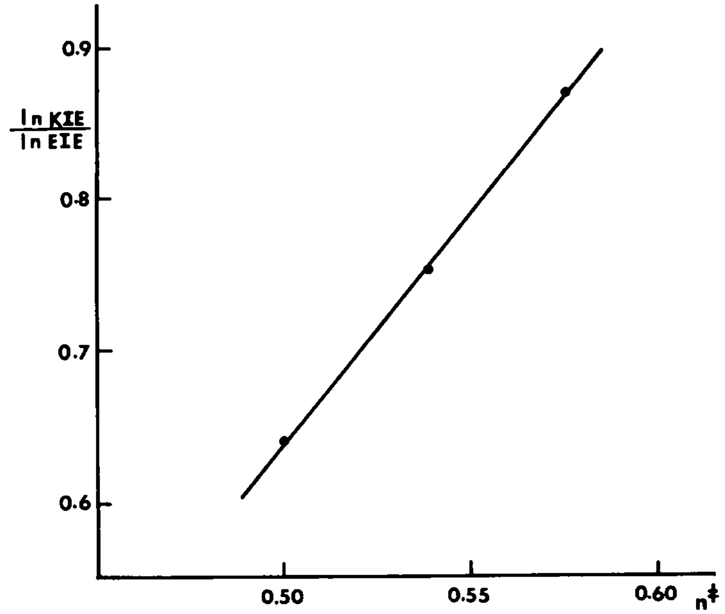
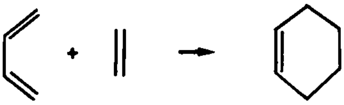


Figure 1. Plot of the kinetic isotope effect expression lnKIE/lnEIE as a function of the bond order of the transition state, $n^{\ddagger}$, for thermoneutral sigmatropic shift reactions of 1,5-hexadienes.

The fact that $n^{\ddagger}$ varies with substitution explains why Hammet LFER give a considerable scatter and is consequently inappropriate to interpret the substituent effects in these sigmatropic shift reactions.[2,3] In fact, within the present model a reaction series corresponds to a constant $n^{\ddagger}$ and λ.[6] Clearly these sigmatropic shifts do not constitute a reaction series because $n^{\ddagger}$ varies along the family of substituents.

Cycloaddition Reactions

Cycloaddition reactions are one of the prototype reactions for the Woodward-Hoffmann rules.[16] Reactions which are forbidden in terms of the conservation of orbital symmetry have a zero bond order ($n^{\ddagger}=0$)and consequently, in terms of our model have an energy barrier corresponding to the dissociation energy of the reactive bond in the reactant. The 2 + 4 cycloadditions are thermally allowed processes in supra/supra or antara/antara process[16]



This reaction can be studied in the same way as the sigmatropic shifts.[§] The average stretching force constant for the six effective bonds in the bond-breaking bond-forming process is virtually the same in the reactant and product, $f=3.3\times10^3$ kJ mol^{-1} A^{o-2}; the average bond lengths are $l_r=1.386$ A^o and $l_p=1.503$ A^o. For a concerted process without substituent effects, $n^{\ddagger}=1/2$. With this set of parameters and a reaction free energy of $\Delta G^o=-83.6$ kJ mol^{-1} the estimated energy barrier is $\Delta G^{\ddagger}=126$ kJ mol^{-1}. Although the exact experimental value is not known, Murdoch[4] provides an estimation of $\Delta G^{\ddagger}=125$ kJ mol^{-1}.

In the same way as in the sigmatropic shift reactions, substituents also cause a decrease in $\Delta G^{\ddagger}$ which can be interpreted in terms of an increase in the bond order of the transition state (Table 2). In the calculation we have employed an approximate constant ΔG^o for all the reactions, since experimental values are not available in all cases. This will affect the absolute $n^{\ddagger}$ values, but substituent effects in cycloaddition reactions are also additive similarly to the sigmatropic reactions. The effect of substituents on siphoning electronic density into the transition state makes $n^{\ddagger}\neq0$ and can make partially allowed a forbidden reaction. In fact there are cases where two ethylenes seem to lead to a cyclobutane ring in a forbidden face to face addition.[16,17] Although there is evidence [17] that such reactions may not proceed via a concerted process, it is of significance that they are observed only when the reactant olefins have substituents. Obviously such reactions can only occur with a reasonable rate if the substituents siphon a significant charge into the transition state. For example, for symmetry forbidden 2+2 cycloaddition of olefins, with $n^{\ddagger}=0.1$ corresponding to the observed increase in $n^{\ddagger}$ for effective substituents, $\Delta G^{\ddagger}=240$ kJ mol^{-1}.[§§] This is a large activation energy but is much lower than the bond dissociation energy barrier.

Table 2. Bond distensions and Transition State Bond Orders in 2+4 Cycloaddition Reactions with Cyclopentadiene.

	$\Delta G^{\ddagger}$/kJ mol $^{-1}$ [a]	d/A^o [b]	n [b]	$n^{\ddagger}$
ethylene	125.5	0.624	0.216	0.5
acrylonitrile	100.3	0.572	0.198	0.545
1,1-dicyanoethylene	74.4	0.514	0.178	0.607
1,1,2-tricyanoethylene	68.1	0.499	0.173	0.625
1,1,2,2-tetracyanoethylene	58.1	0.474	0.164	0.658

[a] Ref. 2. [b] $f=3.3\times10^3$ kJ mol^{-1} A^{o-2}, $l=2.889$ A^o, $\Delta G^o = -83.6$ kJ mol^{-1}.

[§] Only for first order processes are the rates independent of the standard state. One way to eliminate such a difficulty is to consider the rate of reaction within a precursor complex. However the apparent activation free energy with respect to the reagents is independent of the value of the preequilibrium constant. Under this assumption the reaction is strictly not a concerted process and this can slightly decrease $n^{\ddagger}$. However for weak complexes this effect can be neglected.

[§§] For the estimation of $\Delta G^{\ddagger}$ we have considered Morse oscillators, $d=-(1/\beta)\ \ln\{1-[(\Delta G^{\ddagger}-\Delta G^o)/De]^{1/2}\}\ -(1/\beta)\ \ln\{1-[\Delta G^{\ddagger}/De]^{1/2}\}$, where De is the dissociation energy and β the Morse parameter. In the calculations we have employed $De=330$ kJ mol^{-1}, $\beta=2.24$ A^{o-1}, and $\Delta G^o=-84$ kJ mol^{-1}.

Concluding Remarks

In the past, several investigators[18] have tried to generalize Marcus-BEBO equation[8] by introducing in addition to the single reaction coordinate of Marcus, a second coordinate, needed when reactions involve more than merely the rupture of one bond and formation of another. This is a reflection of the limitations of the Marcus theory on describing the progress of a reaction in terms of just one progress variable. The present model is much more flexible than the model of Marcus, because it adds to it two new independent variables $n^{\ddagger}$ and λ. Under these conditions it is possible to describe the progress of the sigmatropic shift and cycloaddition reactions in terms of one progress variable, as for the simpler processes. Marcus theory, which is a particular case of the present model, breaks down when the bond order of the transition state varies with the nature of the reaction and/or when the effect of the configuration entropy is significant. The cases under study were examples of the former situation.

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