Activation hardness and sigmatropic shifts

N K Ray & R C Rastogi
Chemistry Department, University of Delhi, Delhi 110 007
Received 7 July 1993; revised 2 September 1993

Modes of sigmatropic shifts have been examined from a consideration of the hardness parameters of the transition states. The results obtained are in agreement with the well known Woodward-Hoffmann rules. Change in chemical potential has also been examined for the reaction path.

The concepts of electronegativity and hardness and softness of chemical species have drawn a lot of attention in recent years. Hardness $\eta$ of a chemical species is defined as $\eta = (I_{P} - E_{A})/2$ where $I_{P}$ and $E_{A}$ are respectively its ionization potential and electron affinity. Some attempts have been made recently to use $\eta$ as an index of chemical reactivity. Zhou and Parr have defined and used activation hardness for describing orientation in aromatic electrophilic substitution. Ray has used the activation hardness to derive the Woodward-Hoffmann rules for the modes of electrocyclic ring closures of even linear polyenes. We have made an attempt here to use the same concept of activation hardness to understand the modes of sigmatropic shifts (Fig. 1) and the results are reported in this communication.

Method

A sigmatropic shift of order $[i, j]$ is defined as the migration of a $\sigma$ bond, flanked by one or more $\pi$-electron systems, to a new position whose termini are $i-1$ and $j-1$ atoms removed from their original bonded loci, in an uncatalysed intramolecular process. Woodward-Hoffmann rules can be summarized as follows:

<table>
<thead>
<tr>
<th>Thermal</th>
<th>Photochemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[1,4n+1]$ shift:</td>
<td>suprafacial</td>
</tr>
<tr>
<td>$[1,4n+3]$ shift:</td>
<td>antarafacial</td>
</tr>
</tbody>
</table>

where $n$ is an integer. For example a $[1,5]$ shift will be suprafacial under thermal condition while a $[1,7]$ shift will be antarafacial in nature under the same condition.

It is well known that the modes of sigmatropic shifts, both $[1,4n+1]$ and $[1,4n+3]$, can be satisfactorily described in terms of idealized models, i.e., $4n+1$ and $4n+3$ polyene radicals. Following Zhou and Parr, the activation hardness ($\Delta \eta$) can be written as,

$$\Delta \eta = \eta_R - \eta_T = (E_{\text{LUMO}}^R - E_{\text{HOMO}}^R)/2 - (E_{\text{LUMO}}^T - E_{\text{HOMO}}^T)/2$$

... (1)

where $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ stand respectively for the energy of the highest occupied and lowest unoccupied molecular orbitals and the symbols $R$ and $T$ represent the reactant and the transition state.

Equation 1 can be rewritten as,

$$\Delta \eta = (E_{\text{LUMO}}^R - E_{\text{HOMO}}^R)/2 - (E_{\text{LUMO}}^T - E_{\text{HOMO}}^T)/2 = (\Delta E_{\text{LUMO}} - \Delta E_{\text{HOMO}})/2$$

... (2)

In the framework of HOMO method, following Coulson and Longuet-Higgins, one can approximate,

$$\Delta \eta = (\Delta E_{\text{LUMO}} - \Delta E_{\text{HOMO}})/2 = (C_{\text{HOMO}} C_{\text{HOMO}} - C_{\text{LUMO}} C_{\text{LUMO}}) \beta_{rs}$$

... (3)

where $C_{\text{HOMO}}$ is the coefficient of the atomic orbital $r$ in the HOMO and $\beta_{rs}$ is the resonance
integral for the interacting atoms r and s. Using Eq. 3, one can write,
\[ \Delta \eta^s = (C_{HOMO,r} C_{HOMO,s} - C_{LUMO,r} C_{LUMO,s}) \beta^s_{rs} \]  
(4)
and
\[ \Delta \eta^a = (C_{HOMO,r} C_{HOMO,s} - C_{LUMO,r} C_{LUMO,s}) \beta^a_{rs} \]  
(5)
where the superscripts a and s respectively refer to antarafacial and suprafacial transformations. Equation 6 can be written using Eqs 4 and 5,
\[ \Delta \eta^a - \Delta \eta^s = [C_{HOMO,r} C_{HOMO,s} - C_{LUMO,r} C_{LUMO,s}] (\beta^a_{rs} - \beta^s_{rs}) \]  
(6)
Using the first equality of Eq. 1 and Eq. 6, one obtains
\[ \eta^a_{rs} - \eta^s_{rs} = [C_{HOMO,r} C_{HOMO,s} - C_{LUMO,r} C_{LUMO,s}] (\beta^a_{rs} - \beta^s_{rs}) \]  
(7)
\( (\beta^a_{rs} - \beta^s_{rs}) \) is a positive term since \( \beta^a_{rs} \) is positive (see Fig. 1) and \( \beta^s_{rs} \) is negative. Consider a [1,4n+1] thermal migration. The HOMO is the 2n+1 th MO with 2n (even) number of nodes, and hence the first product term within square brackets in Eq. 7 is positive while the 2nd product term is negative. In other words, the term within the square brackets will make a net positive contribution. Consequently, the term \( (\eta^a_{rs} - \eta^s_{rs}) \) in Eq. 7 for a [1,4n+1] thermal migration is a positive quantity implying a harder transition state for the suprafacial process. Zhou and Parr \( ^5 \) have observed earlier that “a transition state with large HOMO-LUMO gap, or hardness is more stable than one with a small gap, and therefore energetically easier to reach.” Hence, a thermal [1,4n+1] sigmatropic shift will prefer the suprafacial mode. [1,4n+1] photochemical shifts can be easily described by noting that in the first excited state the HOMO is the 2n+2 th MO with odd number of nodes and 2n+3 th MO is the LUMO with even number of nodes. Under such circumstances the terms within the square brackets in Eq. 7 will contribute a net negative term which in turn will give a harder transition state for the antarafacial migration. Following along above lines, it can be shown that for a [1,4n+3] sigmatropic shift the thermal process will be antarafacial while the photochemical process will be suprafacial in nature. It should be noted that no attempt has been made to include steric effects that may sometimes dictate the feasibility of a particular mode for a sigmatropic reaction. Although antarafacial shift for a [1,4n+1] thermal sigmatropic shift is allowed, such reactions are quite uncommon because of the severe geometrical requirements and distortion of the carbon framework, with concommitant impairment of coupling within the \( \pi \)-system.

For the sake of completeness we have also examined here the change in chemical potential (\( \Delta \mu \)) in sigmatropic shifts. Chemical potential \( \mu \) is defined as \( \mu = (IP + EA)/2 \) and in the framework of molecular orbital theory it can be written as,
\[ \Delta \mu = (E_{HOMO} + E_{LUMO})/2 \]  
(8)
Following along the lines mentioned earlier in this communication, it is possible to show that,
\[ \Delta \mu = (\mu^a - \mu^s) = (E^T_{HOMO} + E^R_{LUMO})/2 \]
\[ - (E^R_{HOMO} + E^T_{LUMO})/2 = (E_{LUMO} - E_{LUMO})/2 \]
\[ + (E^T_{HOMO} - E^R_{HOMO})/2 = \Delta E_{LUMO} + \Delta E_{HOMO}/2 \]
\[ = [C_{HOMO,r} C_{HOMO,s} + C_{LUMO,r} C_{LUMO,s}] \beta_{rs} \]  
(9)
Using Eq. 9, one can write
\[ \Delta \mu^a - \Delta \mu^s = (\beta^a_{rs} - \beta^s_{rs}) \]  
(10)
where \( \mu^a \) and \( \mu^s \) are respectively the chemical potentials of the transition states associated with the antarafacial shift and suprafacial shift. As has been mentioned earlier, the term \( (\beta^a_{rs} - \beta^s_{rs}) \) is always positive. For a [1,4n+1] thermal shift, the product terms within the square brackets of Eq. 10 can be shown \( ^{11} \) to be positive and this would imply \( \mu^a > \mu^s \). For a [1,4n+3] thermal shift, product terms within the square brackets of Eq. 10 can be shown to be negative and this would lead to \( \mu^a < \mu^s \).

It may be of interest to compare the energy barriers \( (E_a) \) for the antarafacial and suprafacial shifts. Using the frontier orbital concept \( ^{12} \) within HMO framework, one can approximate
\[ E_a = E_T - E_R = \frac{E^T_{HOMO} + E^R_{LUMO}}{2} \]
\[ = 2C_{HOMO,r} C_{HOMO,s} \beta_{rs} \]  
(11)
where, as mentioned earlier, \( \beta_{rs} \) is the resonance integral for the interaction between \( r \) and \( s \) atoms of the polyene. Using Eq. 11, one obtains
\[ E^a_a - E^s_a = 2C_{HOMO,r} C_{HOMO,s} (\beta^a_{rs} - \beta^s_{rs}) \]  
(12)
where the superscripts a and s respectively stand for the antarafacial and suprafacial shifts. For a thermal [1,4n+1] shift, the HOMO is the 2n+1 th MO with 2n (i.e. even) nodes and this will lead
to a positive value for the product term of the coefficients in Eq. 12 implying a greater barrier for the antarafacial shift. In other words, suprafacial mode will be the preferred mode of shift. For a [1, 4n + 3] thermal shift the HOMO is the 2n + 2 th MO with 2n + 1 (i.e. odd) nodes and this will lead to a negative value for the product term of the coefficients in Eq. 12. This in turn will imply a greater barrier for the suprafacial process. Hence, antarafacial process will be the preferred mode. Photochemical shifts can be easily described by noting that the HOMO for a [1,4n + 1] shift is the 2n + 2 th MO. Similarly, for a [1,4n + 3] photochemical shift the HOMO is the 2n + 3 th MO. It is important to note that a harder transition state does indeed correspond to a lower energy of activation inspite of the fact that $\mu_T^s - \mu_T^a$ is not equal to zero. Here we may point out that Eqs 3, 9 and 11, respectively are only approximate definitions for $\Delta \eta$, $\Delta \mu$ and $E_a$.

It is very heartening to see that use of the simple concept of activation hardness can lead to the derivation of the famous Woodward-Hoffman rules\(^8\).

**Acknowledgement**

Thanks are due to Prof. R.G. Parr for his kind interest in the work and some valuable discussion. We thank the referee for valuable comments.

**References**

11. Using analytic expression for $C_{ir}$, one can show that for a thermal [1,4n + 1] shift,
   \[ C_{HOMO}C_{HOMO} + C_{LUMO}C_{LUMO} \]
   \[ = M^2 \sin^2(T) \]
   \[ = M^2 \sin^2 \left( \frac{(2n + 2)\pi}{4n + 2} \right) \]
   For a thermal [1,4n + 3] shift,
   \[ C_{HOMO}C_{HOMO} + C_{LUMO}C_{LUMO} \]
   \[ = N^2 \sin^2(S) - 1 \]
   \[ = N^2 \sin^2 \left( \frac{(2n + 3)\pi}{4n + 3} \right) \]
   M and N are the normalization constants of the molecular orbitals.