ESTIMATION OF THE DIFFERENCE IN ACTIVATION ENERGY BETWEEN WOODWARD-HOFFMANN ALLOWED AND FORBIDDEN REACTIONS

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Recently, Brauman and Golden[2] have reported an activation energy of 26 kcal/mole for the reaction of bicyclo[2.1.0]pent-2-ene isomerizing to cyclopentadiene. They have also estimated that, in the absence of strain, the activation energy difference between a Woodward-Hoffmann[3] allowed and a Woodward-Hoffmann forbidden process is 15 kcal/mole. They based this estimate on comparisons of their reaction and the two similar Woodward-Hoffmann forbidden reactions, the isomerization of bicyclo[3.2.0]hept-6-ene to 1,3-cycloheptadiene[4] and the isomerization of bicyclo[4.2.0]oct-7-ene to 1,3-cyclooctadiene,[5] with the corresponding Woodward-Hoffmann allowed process, the isomerization of cyclobutene to 1,3-butadiene.[6]

Brauman and Golden propose that

$$\Delta H^{\ddagger} = \Delta H_f^{\ddagger} - \Delta H_f^{(gs)} = BE(gs) - BE^{\ddagger}$$

where BE(gs) represents the bond dissociation energy of those bonds broken in going to the transition state, and $BE^{\ddagger}$ is the bonding energy of those bonds which are partially formed in the transition state. They calculate BE values from the equation

$$BE = UBE - SE$$

where UBE is the bond dissociation energy of a similar open chain system, and SE is the strain energy of the compound. Thus

$$\Delta H^{\ddagger} = UBE(gs) - SE(gs) - UBE^{\ddagger} + SE^{\ddagger}$$

They calculate that $UBE^{\ddagger}$ for the Woodward-Hoffmann process is approximately 20 kcal/mole and for the non-Woodward-Hoffmann process is approximately 5 kcal/mole. Thus, they suggest 15 kcal/mole as the difference in the energies of the transition states.

However, because this equation contains strain energies, difficulties arise in dealing

with isomerization reactions since strain energies must contain a contribution from a

theoretical "unstrained" molecule. These difficulties are illustrated as follows. Cyclo-

butene has a strain energy of 28.5 kcal/mole,[7] and butadiene has a strain energy of -4 kcal/

mole,[7] thus, based on strain energies, one would expect a difference between the compounds

of about 32 kcal/mole. However, as the heat of formation of cyclobutene is +37.5 kcal/mole[8]

and that of butadiene is +26.0 kcal/mole,[9] these compounds actually differ in energy by only

11.5 kcal/mole.

In view of the above discrepancy, we feel that the following expression is somewhat

more rigorous in estimating energies.

$$\Delta H^{\ddagger} = \Delta H^{\ddagger}_{unst.\ rxn.} - \Delta\Delta H_f\ geom$$

Here, $\Delta H^{\ddagger}_{unst.\ rxn.}$ is the activation energy if the transition state geometry were of the same

energy as the ground state, and $\Delta\Delta H_f geom$ is the difference between the heat of formation of

the ground state, and of the assumed geometry of the transition state. In column I of Table II

below are listed the values obtained by assuming, as Brauman and Golden did, that the

transition state has the geometry of the product diene. The results show that in the absence

of strain assistance, the non-Woodward-Hoffmann process has a transition state 12-22 kcal

higher in energy.

However, the assumption that the transition state has the structure of the product

diene violates a well accepted principle, namely the postulate of Hammond,[10] which states

that the structure of the transition state should resemble the reacting species of higher energy.

The results in column II of Table II are based on the assumption that $\Delta\Delta H_f$ is 1/2 the energy

of isomerization and in column III $\Delta\Delta H_f$ is assumed to be 1/3 the energy of isomerization.

Both these columns give the value of the activation energy difference between the allowed and

forbidden reactions for the 7 and 8 carbon compounds to be 11-14 kcal/mole. Brauman and

Golden mention that the strain energy of the bicyclo[2.1.0]pent-2-ene is probably higher than

their estimate, so the number for that compound is questionable.

Another way to arrive at the same conclusion is to consider that the isomerization

energies for the larger ring compounds and for cyclobutene itself are all approximately equal.
Thus, one can assume that the transition state occurs at the same place along the reaction
coordinate and one can directly compare activation energies. This results in an energy
difference of 10-12 kcal/mole. As Brauman and Golden state, the energy difference must
be greater than 4 kcal/mole to account for the observed stereospecificity. It has been just
shown that the difference in these cases is 10-14 kcal/mole, and probably closer to 10, since
that number is obtained when the energies of isomerization of the allowed and forbidden pro-
cesses are most closely matched.

<div align="center">Table I</div>

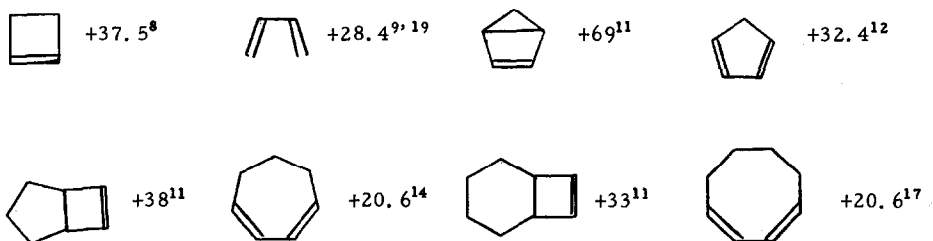<div align="center">Heats of Formation of Compounds</div>

<div align="center">Table II</div>

<div align="center">Activation Energies</div>

Compound	$\Delta H^{\ddagger}$	$\Delta\Delta H_f$	$\Delta H^{\ddagger}_{u.r.}$	$\Delta\Delta H_f$	$\Delta H^{\ddagger}_{u.r.}$	$\Delta\Delta H_f$	$\Delta H^{\ddagger}_{u.r.}$
		I			II		III
2.1.0	26[2]	37	63	18	44	12	38
3.2.0	44[4]	17	61	8	52	5	49
4.2.0	42[5]	12	54	6	48	4	46
cyclobutene	32[6]	9	44	5	37	3	35

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11. This value is calculated from the strain energies listed in reference 2. Those authors refer to S. W. Benson et al., Chem. Revs., in press.

12. This value is calculated from the heat of formation of cyclopentane (-18.4 kcal/mole[9] and the gas phase heat of hydrogenation of cyclopentadiene (50.9).[13]

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14. This value is calculated from the heat of formation of cycloheptane (-28.3)[15] and the gas phase heat of hydrogenation of 1,3-cycloheptadiene.[16]

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17. This value is calculated from the heat of formation of cyclooctane (-29.8)[15] and the liquid phase heat of hydrogenation of 1,3-cyclooctadiene (49.04),[18] corrected for the difference between liquid and gas phase heats of hydrogenation for 1,3-cycloheptadiene (1.4 kcal).

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