Woodward−Hoffmann Rule in the Light of the Principles of Maximum Hardness and Minimum Polarizability: DFT and Ab Initio SCF Studies

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Abstract: Electrocyclic transformation between *cis*-butadiene and cyclobutene has been studied at the HF and DFT levels with 6-311G** basis sets. The disrotatory stationary point with two imaginary vibrational frequencies is associated with higher energy and polarizability values and a smaller hardness value in comparison to those of the symmetry-allowed conrotatory transition state for the thermolysis of cyclobutene. For *cis*-butadiene, the actual minimum energy structure is of C_2 symmetry. *cis*-Butadiene and cyclobutene have energy and polarizability values lower than those of both stationary points, and the respective hardness values are higher than the stationary point hardness values.

Introduction

The concept of chemical hardness[1−3] was introduced by Pearson through his hard−soft acids and bases (HSAB) principle which states that,[1−4] "hard likes hard and soft likes soft". Another important related hardness principle also proposed by Pearson[5] is the maximum hardness principle (MHP)[1,6,7] which states that,[6] "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". It has been shown[8] that the validity of the HSAB principle somehow demands that of the MHP. Molecular vibration and internal rotation, different types of chemical reactions, aromaticity, stability of the closed-shell species, clusters with a magic number of atoms, various time-dependent problems, etc. are successfully studied[1,7] using the MHP.

The maximum hardness criterion complements the minimum energy criterion for stability. In general, a stable state (minimum energy configuration) or a favorable process is associated[1,7] with the maximum hardness and a transition state with the minimum hardness.[9]

The hardness (η) has been defined within the density functional theory (DFT) as the second derivative of the total electronic energy (E) with respect to the number of electrons (N) at constant external potential $\upsilon(\mathbf{r})$,

$$\eta = \frac{1}{2}\left[\frac{\partial^2 E}{\partial N^2}\right]_{\upsilon(\mathbf{r})} \tag{1}$$

The external potential $\upsilon(\mathbf{r})$ is the potential due to a set of nuclei as well as the external field.[10] An operational definition of hardness is obtained by approximating the above derivative in terms of the ionization potential (I) and electron affinity (A) of the system as

$$\eta = \frac{(I - A)}{2} \tag{2}$$

which can be further approximated by making use of the Koopmans' theorem as[3]

$$\eta = \frac{(\epsilon_L - \epsilon_H)}{2} \tag{3}$$

where ϵ_L and ϵ_H are the lowest unoccupied and highest occupied molecular orbital energies, respectively.

Within the density functional theory the complete characterization of an N-particle system needs only N and $\upsilon(\mathbf{r})$.[3,10] The change of the system due to a change in N at constant $\upsilon(\mathbf{r})$ can be measured by η. On the other hand, the linear response function of perturbation theory takes care of the changes of the system due to the variation of $\upsilon(\mathbf{r})$ at constant N. In the case that the variation in $\upsilon(\mathbf{r})$ is produced by a weak electric field, the polarizability (α) may be used as a measure of the corresponding linear response. Hence, it is known that an inverse relationship between α and η exists.[11] This has prompted us to propose a minimum polarizability principle (MPP),[12] which

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states that “the natural direction of evolution of any system is toward a state of minimum polarizability”.

Reaction mechanisms of the concerted stereospecific reactions are best understood through the Woodward−Hoffmann rule[13] based on the conservation of the orbital symmetry during such a reaction process. In electrocyclic reactions, the reason for the observed stereospecificity is that the groups bonded to the breaking bond all rotate in the same sense during the ring-opening process. This motion, in which either all rotate clockwise or all rotate counterclockwise, is called the *conrotatory* mode. If these groups rotate in opposite direction during the cyclization process, the mode is called *disrotatory*. An axis of symmetry (C_2) and a plane of symmetry (C_s) are preserved for a conrotatory process and a disrotatory process, respectively. Which process would be favored depends on the number of π-electrons in the system. In general, conrotatory and disrotatory motions are favored for systems with $4n$ and $(4n + 2)$ π-electrons, respectively. It may be noted[13] that if conrotatory motion is preferred for a given thermal reaction, the corresponding disrotatory path will be photochemically allowed. The Moebius−Hueckel treatment of pericyclic reactions developed by Zimmerman[14] also explains this kind of concerted stereospecific reaction without requiring symmetry. One of the simplest possible concerted reactions, explained by those rules, is the thermolysis of cyclobutene to *cis*-butadiene. Hartree−Fock, semiempirical, and ab initio calculations[15−18] as well as DFT and valence bond (VB) studies[19,20] have been performed for this electrocyclic isomerization. Since the calculations of Breulet and Schaefer (BS)[18] provide one of the most elegant theoretical explanations of the thermolysis of cyclobutene, we mainly rely on their results. For a recent exhaustive ab initio study on the photocyclization of butadiene, where the disrotatory path is allowed according to the Woodward−Hoffmann rule, see ref 21.

From MHP we expect that the hardness values of the transition states (TS) will be lower than the hardness values of both cyclobutene and *cis*-butadiene, and the disrotatory TS will have a smaller η value, in comparison to the η value of the corresponding conrotatory TS associated with the thermal isomerization of cyclobutene. On the other hand, from MPP we expect that the polarizability values of the TS will be greater than the polarizability values of both, cyclobutene and *cis*-butadiene, and the disrotatory TS will have a larger α value in comparison to the α value of the corresponding conrotatory TS. In general, when the corresponding quantities of two possible TSs are compared, the TS attached to a symmetry-allowed path will possess lower energy, larger hardness, and smaller polarizability values, whereas the TS associated with the symmetry forbidden pathway will have higher energy, smaller hardness, and higher polarizability values. In other words, both hardness and polarizability correlate with forbiddenness. This is expected, because Zimmerman’s works[14] showed that degeneracies are characteristic of forbidden reactions, and both, hardness and polarizability, are related to energy differences between the ground and excited states.

To verify this prognosis in the present work we calculate hardness and polarizability values of cyclobutene, *cis*-butadiene, and the two TS’s (conrotatory and disrotatory) through single-point HF and DFT calculations with Breulet and Schaefer[18] geometries, and also optimize the geometry wherever necessary.

Computational Details

Equilibrium and transition state geometries of various species involved in the thermochemical electrocyclic isomerization of cyclobutene to *cis*-butadiene are taken from the two-configuration SCF result of Breulet and Schaefer.[18] Single-point calculations for all these species with Breulet and Schaefer geometries[18] have been performed at the Hartree−Fock level as well as within density functional theory. For the DFT calculations B3LYP[22,23] exchange-correlation functionals have been used. Unless otherwise specified the basis set used is 6-311G**. Hardness values have been calculated using eq 3. In the DFT calculations Kohn−Sham orbital energy[24] values are used (eq 3). Although these orbitals are different from the canonical molecular orbitals the orbital energy values are known to be similar.[3,25] Frequency values are calculated at both HF and DFT levels mainly to check the number of imaginary frequencies (NIMAG). For *cis*-butadiene geometry optimization and the pertaining frequency calculation have been performed at HF/6-311G** and B3LYP/6-311G** levels. The dipole polarizabilities have been calculated using the B3LYP method to include the most important correlation effects. They are calculated as a numerical derivative of the dipole moment. The basis set developed by Sadlej[26] has been used. They are specially suited for dipole polarizability calculations. All calculations have been carried out with the GAUSSIAN 94 program.[27]

Results and Discussion

Total energy, hardness, and (imaginary) frequency values for cyclobutene, *cis*-butadiene, conrotatory TS, and disrotatory TS obtained at the HF/6-311G** and B3LYP/6-311G** levels through single-point calculations using Breulet and Schaefer geometries[18] are presented in Table 1. Also given in this table are the number of imaginary frequencies (NIMAG) of these species. For any quantity, the first entry corresponds to HF calculation and the second one is from the DFT calculation. The energy values for both TSs are much above the corresponding values of the reactant and the product at both levels of calculations. The activation energy for the conrotatory process (36.4 kcal/mol) calculated at the B3LYP level compares well with the corresponding experimental value[28] (32.9 kcal/mol). However, it is to be noted that the energy difference involving the disrotatory process should be calculated at a multiconfigu-

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Table 1. Total Energy, Number of Imaginary Frequencies (NIMAG), Imaginary Frequency, and Hardness Values for the Predicted Stationary Points for the Isomerization Reaction of Cyclobutene[a]

species, PG	NIMAG	−energy	η	frequency
cyclobutene, C_{2v}	0	154.9308	6.91	0
	0	156.0113	3.61	0
cis-butadiene, C_{2v}	1	154.9516	5.70	160.2 i
	1	156.0313	2.57	255.7 i
conrotatory, C_2 TS	1	154.8523	5.43	922.7 i
	1	155.9532	2.42	780.2 i
disrotatory, C_s TS	2	154.7564	3.27	1174.8 i 208.7 i
	2	155.8828	0.912	1037.5 i 212.5 i

[a] Energy in atomic units and hardness values in eV. Frequency values in cm $^{-1}$. NIMAG is the number of the predicted imaginary frequencies for each stationary point. For each molecule single point calculations have been performed at the HF/6-311G** (first entry) and B3LYP/6-311G** (second entry) levels using the geometries from Breulet and Schaefer.[17] Point groups (PG) that different species belong to are specified in the first column.

Table 2. Total Energy, Hardness, Diagonal Polarizability Components, and the Mean Value of the Polarizability of the Predicted Stationary Points for the Isomerization Reaction of Cyclobutene[a]

species, PG	−energy	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	η
cyclobutene, C_{2v}	155.9940	38.74	54.50	50.00	47.70	3.36
cis-butadiene, C_{2v}	156.0120	36.83	74.20	52.99	54.70	2.48
conrotatory, C_2 TS	155.9340	39.38	74.93	56.06	56.80	2.35
disrotatory, C_s TS	155.8650	42.26	58.60	112.70	71.20	0.91

[a] Energy (atomic units), hardness (eV), and polarizability (atomic units) values are from B3LYP calculations using the Sadlej basis set. Point groups (PG) that different species belong to are specified in the first column.

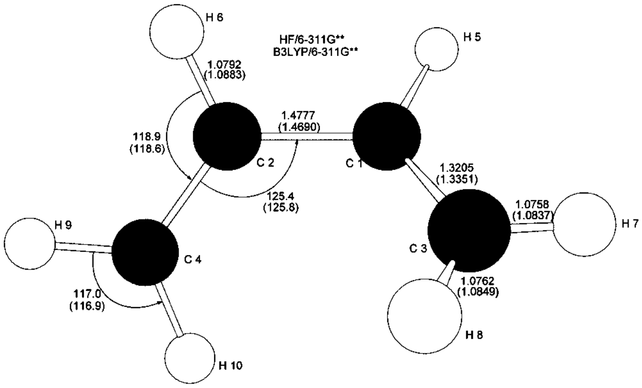

Figure 1. Optimized geometry of *cis*-butadiene (C_2). For details see text. The dihedral C1−C2−C3−C4 angle is −40.3° and −32.9° at HF/6-311G** and B3LYP/6-311G** levels of theory, respectively.

rational level. This should be done but could not be done in the present work. The energy values of the disrotatory process showed here only indicate the correct trend but they are not expected to be compared with experimental values.

It is clear from the respective NIMAG values that cyclobutene with C_{2v} symmetry is a minimum energy structure and the conrotatory TS with a single imaginary frequency is a real TS. However, as argued by Breulet and Schaefer,[18] the TS for the disrotatory motion is distorted from C_s symmetry. A stationary point for the disrotatory motion (C_s symmetry pathway) with two imaginary frequencies has been observed, similar to what Breulet and Schaefer[18] obtained. It has been pointed out[18] that a single-configuration wave function may suffice for the study of the conrotatory process but at least a two-configuration wave function is needed for analyzing the disrotatory process. Although the present calculations are at the HF and DFT levels, the geometry of the disrotatory stationary point used here is that of Breulet and Schaeffer which has been optimized with two-configuration SCF calculations.[18] The most intriguing aspect originates from the analysis of structure and vibrational frequencies of *cis*-butadiene. Theoretically obtained geometrical parameters for this molecule could not be compared with the corresponding experimental values mainly because there is no experimental characterization of it.[29] Although there is some indirect experimental evidence that the molecule is nonplanar,[30] almost all electronic structure calculations on it assumed the molecule to be planar. In the present work we notice that the molecule with C_{2v} structure[18] does not correspond to minimum energy because it has one imaginary vibrational frequency (160.2 i/HF, 255.7 i/DFT). For this reason, we have optimized the geometry of *cis*-butadiene at HF/6-311G** and DFT/6-311G** levels which will be discussed later in this section.

The hardness values for both the conrotatory TS and the disrotatory stationary point are less than the corresponding values of the reactant and the product, as expected from MHP. The disrotatory process being symmetry-forbidden, according to the Woodward−Hoffmann rule,[13] the energy of the corresponding TS is above that of the conrotatory TS. It is heartening to note that both HF and DFT level calculations provide the smallest hardness values for the disrotatory TS as would have been predicted by the MHP. In passing we note that the η value for *cis*-butadiene is smaller than that of cyclobutene. It may be due to the fact that the structure of *cis*-butadiene used here is associated with two negative eigenvalues for the corresponding force constant matrix. Whether the η value increases with the geometry optimization will be analyzed later in this section.

In Table 2 the energy values, hardness, diagonal dipole polarizability components, and the mean value of polarizability [$\langle\alpha\rangle = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$] for the four states involved in the electrocyclic transformation of cyclobutene to *cis*-butadiene are displayed. First, it is worth observing that the hardness values do not change by a significant amount by using Sadlej's basis set. Second, the mean value of the dipole polarizability follows the postulated minimum polarizability principle: the polarizabilities for both the conrotatory TS and the disrotatory stationary point are greater than the corresponding values of the reactant and product ground states. The symmetry-allowed conrotatory TS is less polarizable than the symmetry-forbidden disrotatory stationary point, as expected from the MPP.

The optimized geometry of *cis*-butadiene is shown in Figure 1. In this figure the DFT/6-311G** values are given in parentheses and other values are from the HF/6-311G** calculation. The related geometrical parameters are listed in Table 2, where they are compared with the other reported theoretical results.[15−17] The fully optimized geometry has a C_2 symmetry in the present calculation unlike all other previous calculations where a C_{2v} symmetry was obtained. The bond lengths and bond angles in *cis*-butadiene (C_2) from the present calculations compare well with those reported by Bock et al.[17] from their fully optimized 4-31G SCF calculation. The optimization procedure used to obtain the C_2 structure of *cis*-butadiene was performed under the constraint that the bond distances and bond angles in each branch around the principal

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Table 3. Geometical Parameters of the Optimized *cis*-butadiene (C_2) Structure[a]

parameter	present research		Breulet and Schaefer[b]	MINDO/2[c]	HF/4-31G[d]
	HF/6-311G**	DFT/ 6-311G**			
bond lengths					
C_1C_3	1.3205	1.3351	1.3490	1.3200	1.3230
C_3C_4	1.4777	1.4690	1.4580	1.4600	1.4720
C_1H_1	1.0758	1.0837	1.0730	1.0940	1.0780
C_1H_3	1.0764	1.0849	1.0740	1.0940	1.0790
C_3H_5	1.0792	1.0883	1.0760	1.0940	1.0790
angles					
$C_1C_3C_4$	125.4	125.8	127.6	127.1	127.1
$C_1C_3H_5$	118.9	118.6	117.6	118.6	118.1
$H_1C_1H_3$	117.0	116.9	116.4	110.8	115.9
dihedral angles					
$C_1C_3C_4C_2$	−40.3	−32.9			
$H_1C_1C_3H_5$	−2.2	−2.6			
$H_3C_1C_3H_5$	177.1	176.5			

[a] Bond distances in angstrom units and angles in degrees. All other structures[14−17] are of C_{2v} symmetry. [b] From ref 17. [c] From ref 14. [d] From ref 16.

Table 4. Optimized Quantities for *cis*-Butadiene (C_2)[a]

method	NIMAG	−energy	η	$\langle\alpha\rangle$
HF/6-311G**	0	154.9551	6.28	51.21
DFT/6-311G**	0	156.0329	2.83	53.90

[a] Energy and polarizability values in atomic units and hardness values in eV.

axis of symmetry of the structure shown in Figure 1 was equal to each other. The C1−C2−C3−C4 dihedral angle was allowed to relax. The resulting dihedral angle was found to twist the molecule out of plane −40.3° and −32.9° at the HF/6-311G** and B3LYP/6-311G** levels of theory, respectively.

Table 3 comprises various optimized quantities for *cis*-butadiene (C_2). The zero NIMAG value (both HF and DFT calculations) confirms that the C_2 symmetry corresponds to the real minimum energy structure. A similar result was obtained by Sakai[21] in a different context with a different level of computation. In Table 4 we present the various quantities of *cis*-butadiene with C_2 symmetry. Energy values (HF and DFT) go down and hardness values go up upon optimization (albeit not above the η values of cyclobutene), as expected. Also, the mean value of the polarizability decreases due to the geometry optimization as would have been predicted by the MPP.

Concluding Remarks

Ab initio and DFT calculations have vindicated that the symmetry-allowed conrotatory transition state will be of lower energy, harder, and less polarizable than the corresponding symmetry-forbidden disrotatory stationary point associated with the electrocyclic isomerization of cyclobutene to *cis*-butadiene, as expected from the maximum hardness and minimum polarizability principles. The reactant and the product of this concerted stereospecific reaction possess smaller energy and polarizability values and larger hardness values than those of both stationary points.

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