The Hammond Postulate and the Principle of Maximum Hardness in Some Intramolecular Rearrangement Reactions

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In this paper we use the energy, the electronic chemical potential, and the molecular hardness together with a similarity index and a thermodynamic index to rationalize the behavior of various intramolecular rearrangement reactions in terms of the Hammond postulate (HP) and the principle of maximum hardness (PMH). The following results have been obtained: (a) in general, Hammond and anti-Hammond reactions satisfy the PMH in the sense that they present an opposite behavior for the energy and hardness profile along the reaction coordinate; (b) in Hammond reactions the hardest species among reactants and products corresponds to the most stable one; and finally, (c) in anti-Hammond reactions the less stable species among reactants and products is the hardest one.

1. Introduction

The Hammond postulate[1] (HP) is a useful tool that interrelates the position of the energy barrier on the potential energy surface (PES) with the exo- and endothermicity of a given reaction. It basically states that if the transition state (TS) is near in energy to a certain adjacent stable complex, then it is also similar in structure to the same complex. In other words, an exothermic reaction has a reactant-like TS, whereas product-like TSs characterize endothermic processes. The HP is supported by abundant empirical evidence in organic and physical chemistry,[2] and it has been useful for qualitatively predicting the effects of substituent changes and external perturbations on the TS geometries.[3] The HP works when slopes and matrixes of force constants associated with reactants and products in an elementary process are not very different.[4,5] It applies to most chemical reactions, although some failures of this postulate have been also reported.[6−8]

In the quest to quantify the HP character of a given reaction different methodologies have been developed.[5,8−11] Among them, the most employed have been those based on the use of quantum molecular similarities. In this case, for a reaction A → B, the so-called structural proximity parameter (β_s) defined by Cioslowski as[9]

$$\beta_s = (d_{A,TS} - d_{B,TS})/d_{A,B} \tag{1}$$

is used. β_s can take any values from −1 to 1. If the reactants A are closer to the TS than the products B, the value of β_s is negative and positive otherwise. Therefore, if one considers an exothermic A→ B process, a negative β_s value means that for this reaction the HP holds.

A possible definition of the distance in eq 1 between the molecular electronic distributions of A and B is given by

$$d_{A,B} = [Z_{A,A} + Z_{B,B} - 2Z_{A,B}]^{1/2} \tag{2}$$

where $Z_{A,B}$ is the quantum molecular similarity measure (QMSM) between molecules A and B as defined by Carbó et al.,[12,13]

$$Z_{A,B}(\Theta) = \int\int \rho_A(\mathbf{r}_1)\Theta(\mathbf{r}_1,\mathbf{r}_2)\rho_B(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{3}$$

$\Theta(\mathbf{r_1},\mathbf{r_2})$ being a positive definite operator depending on two-electron coordinates. Overlap-like QMSM are obtained when the $\Theta(\mathbf{r_1},\mathbf{r_2})$ operator is chosen as the Dirac delta function $\delta(\mathbf{r_1}-\mathbf{r_2})$. Use of the operator $1/r_{12}$ or $1/r^2_{12}$ gives rise to Coulomb-like QMSM and gravitational-like QMSM, respectively.[13] Since the value of the distance given by eq 2 depends on the relative spatial orientation of molecules A and B, their mutual orientation must be optimized in order to maximize their QMSM, which is equivalent to minimize the $d_{A,B}$ value used in the evaluation of the β_s parameter.

Another index that has been used to quantify the Hammond postulate is the so-called Brönsted coefficient β_b that was originally defined by Leffler as[14]

$$\beta_b = \frac{\partial \Delta E^{\ddagger}}{\partial \Delta E^{\circ}} \tag{4}$$

To obtain β_b we use the following equation accounting for the energy barrier ($\Delta E^{\ddagger}$):[11]

$$\Delta E^{\ddagger} = \left[\frac{1}{4}K + \frac{1}{2}\Delta E^{\circ} + \frac{(\Delta E^{\circ})^2}{4K}\right] \tag{5}$$

with $K > 0$ being an intrinsic structural property of the reaction corresponding to the sum of the curvatures of the potential wells associated to reactants and products, and $\Delta E^{o} = [E(P) - E(R)]$ being the overall reaction energy. To add more precision about the definition of the parameter K, it should be mentioned that it has been shown that it is proportional to the average of the force constants associated to the potential wells of reactants and products.[15] It is important to note that eq 5 is structurally

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homogeneous to the Marcus equation originally proposed to characterize electron-transfer processes,[16] and later on used for interpretation of different kinds of chemical reactions.[15,17] The interest of using eq 5 for rationalizing our results is that it leads to a definition of β_b that is physically consistent with the Hammond postulate. On the other hand, it is worth mentioning that eq 5 can also be used to determine the structural parameter K if only energetic parameters are available. Moreover K is associated with the Marcus intrinsic activation energy, an electronic term that contains structural information of reactants and products.

From eqs 4 and 5 we determine β_b:

$$\beta_b = \frac{1}{2} + \frac{\Delta E^\circ}{2K} \tag{6}$$

The Brönsted coefficient can be interpreted as a measure of the degree of resemblance of the TS to the product(s) and takes values typically around $\beta_b \approx 1/2$. For endothermic reactions ($\Delta E^\circ > 0$) the TS will be located closer to the products ($\beta_b > 1/2$); for exothermic reactions ($\Delta E^\circ < 0$) the TS will be closer to the reactants ($\beta_b < 1/2$), thus quantifying the HP.

Note that β_b, a thermodynamic coefficient that depends basically on the reaction energy, is useful to locate the TS with respect to reactants and products in reactions where the HP is satisfied, but it cannot be used to characterize deviations from the Hammond behavior. On the other hand, the similarity index β_s is basically a structural parameter in the sense that it can help to characterize the reactant-like or product-like character of the TS from a structural point of view. Therefore, these two indexes are different in nature but they can be complementary to each other.

On the other hand, Density Functional Theory (DFT)[18] has provided the theoretical basis for concepts that are implicated in the reactivity of chemical species. The electronic chemical potential μ characterizes the escaping tendency of electrons from the equilibrium system and the molecular hardness η can be seen as a resistance to charge transfer. Both are global properties of the system and the characterization of their profiles along a reaction coordinate has been shown to be useful to study new aspects of the progress of chemical reactions.[11]

One major focus of attention in DFT is the principle of maximum hardness (PMH)[19] that asserts that molecular systems at equilibrium tend to the state of highest hardness: TSs are expected to present a minimum value of η. It has been shown that consistency between the PMH and the HP may lead to a better characterization of TSs.[11,20] A formal proof of the PMH was given by Parr and Chattaraj[21] under the constraints that μ and the external potential $v(\mathbf{r})$ must remain constant upon distortion of the molecular structure. However, relaxation of these constraints seems to be permissible, and in particular, it has been found that the PMH still holds even though the electronic chemical potential strongly varies along the reaction coordinate.[11,19] It is important to mention that for a given chemical reaction connecting the change of energy with the change in chemical potential and hardness allows one to discuss thermodynamic and kinetic aspects involved in the process. However, a proper thermodynamic discussion should be addressed in terms of free energies at finite temperature. Since for macroscopic systems at temperature T, the equilibrium state is analogous to the ground state at 0 K, finite temperature definitions of μ and η are implicit in the following discussion.[18]

In what follows we shall analyze the validity of the HP and the PMH in the following series of simple chemical rearrangement reactions:[22] HNC → HCN (R1), HClO → HOCl (R2), HONS → HSNO (R3), H_2SO → HSOH (R4), H_2SeO → HSeOH (R5), F_2S_2 → FSSF (R6), H_3PO → H_2POH (R7), H_3AsO → H_2AsOH (R8), and CH_2SH_2 → CH_3SH (R9). These reactions have been chosen because some of them follow the HP, whereas others exhibit anti-Hammond behavior. Our main goal is to discuss the validity of the HP and the PMH in this series of intramolecular rearrangement reactions and to investigate whether one can safely assume that a reaction that follows the HP will also hold the PMH.

2. Computational Details

The geometries of all molecular systems studied in this work have been fully optimized without symmetry constraints at the Hartree−Fock (HF) level with the 6-31G* basis set[23] through use of the Gaussian 94 package.[24] The algorithm of Gonzalez and Schlegel[25] was used for the computation of the intrinsic reaction path (IRP) at the HF/6-31G* level of theory, with mass-weighted coordinates in order to get a physically meaningful path. Further, the energies of reactants, TSs, and products of each rearrangement reaction, and their HOMO and LUMO orbital energies, chemical potential, and hardness, have been recalculated at the B3LYP/6-31+G* level[26] using the HF/6-31G* optimized geometries (B3LYP/6-31+G*//HF/6-31G*).

The definition of μ and η were given by Parr and Pearson[18,19] and a three-points finite difference approximation leads to the following working definitions of these quantities:

$$\mu = -\frac{1}{2}(\mathrm{IP} + \mathrm{EA}); \quad \eta = \frac{1}{2}(\mathrm{IP} - \mathrm{EA}) \tag{7}$$

IP and EA are the first vertical ionization potential and electron affinity of the neutral molecule, respectively. The Koopmans' theorem (IP $\approx -\epsilon_H$ and EA $\approx -\epsilon_L$) allows one to write μ and η in terms of the energy of frontier HOMO (ϵ_H) and LUMO (ϵ_L) molecular orbitals:

$$\mu = \frac{1}{2}(\epsilon_L + \epsilon_H); \quad \eta = \frac{1}{2}(\epsilon_L - \epsilon_H) \tag{8}$$

Chemical potential and hardness are very well-established quantities that have evoked considerable research activity in the past few years.[18−21] It is worth mentioning that although the numerical values may differ, the overall trends remain unaltered when μ and η are calculated using eqs 7 or 8.[11] In this work, μ and η have been calculated using both eqs 7 and 8. For the calculation of IP and EA values at the B3LYP/6-31+G*//HF/6-31G* level, the energy of the cationic and anionic doublet species has been computed within the unrestricted methodology, while the neutral singlet molecules have been calculated within the restricted formalism. In all cases, the HF/6-31G* optimized geometries of the neutral molecules have been used.

The methodology employed for the calculation of the quantum molecular similarity measures has been the same as in our previous work.[8] In particular, Coulomb-like QMSM have been computed from fitted densities[27] using the Messem program.[28] The Brönsted coefficient has been determined using eq 6 previous calculation of the parameter K from the knowledge of the reaction and energy barriers in eq 5.

3. Results and Discussion

Figure 1 depicts the geometries of reactants, TSs, and products of the nine rearrangement reactions analyzed. Table 1 lists the reaction parameters in which we are interested in this work. As one can see in this table, the energy barriers of all reactions computed at the B3LYP/6-31+G*//HF/6-31G* are positive,

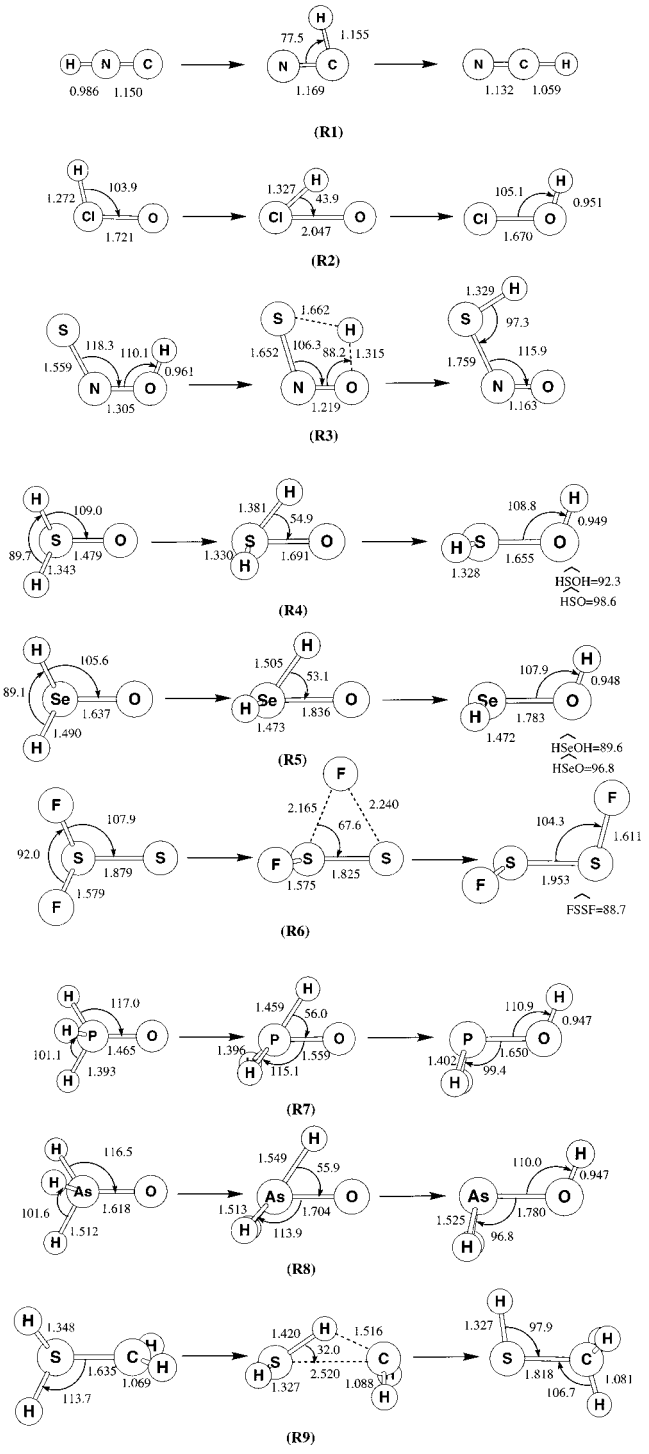

Figure 1. HF/6-31G* optimized geometries for the reactants, transition states, and products of the nine rearrangement reactions analyzed. Bond lengths are given in angstroms and angles in degrees.

except that of reaction R2. At the HF level the energy barrier for the R2 reaction is 14.2 kcal mol^{-1}. Given that the HF barriers are usually too high and the B3LYP ones are somewhat underestimated[29] it is not completely unexpected that the B3LYP/6-31+G*//HF/6-31G* energy barrier for reaction R2 turns out to be negative.

In all reactions studied, reactants and products are defined in such a way that the reaction results to be exothermic. This is the reason in all cases the Brönsted coefficient is lower than 0.5 (see eq 6), indicating that under this criterium the TSs are reactant-like, as expected from the HP.

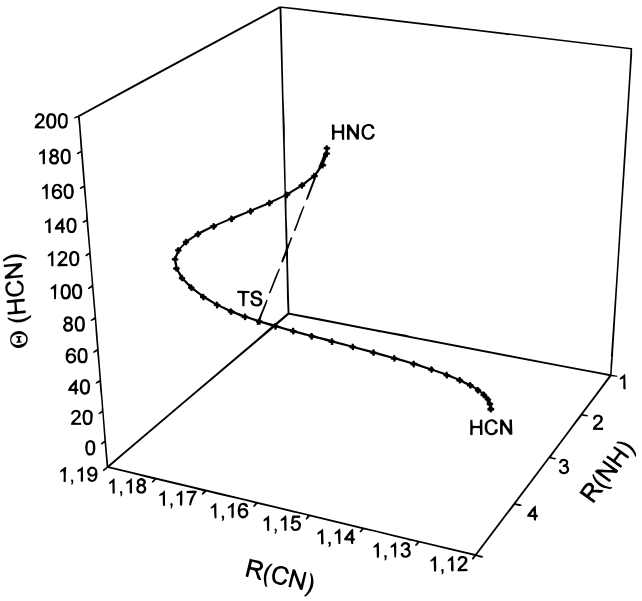

Figure 2. The IRP in mass-weighted coordinates of the rearrangement reaction HNC → HCN reaction computed at the HF/6-31G* level.

In contrast to β_b, different results are obtained when analyzing the β_s values. We find this to be true in five cases $\beta_s < 0$, indicating that these reactions are of Hammond type. However, reactions R4, R5, R7, and R8 present positive values of β_s and therefore, following the β_s criterium, these reactions are of anti-Hammond type. Note that β_s has been defined in terms of the measures of electron-density similarities and therefore one should expect this index to be adequate to characterize the early or late character of TSs structures.

In principle, one could argue that the length of the IRP should be a useful parameter to distinguish the Hammond or anti-Hammond character of a reaction. Larger lengths of the mass-weighted IRP in the way from TS to products than from TS to reactants should be indicative of Hammond behavior in exothermic reactions. As one can see in Table 1 this is true for most reactions. The Hammond type reactions have larger R_X distances from the TS to products, while the anti-Hammond type reactions present larger R_X distances from the TS to reactants, with the exception of R1, R2, and R8. We have analyzed the particular case of the HNC → HCN reaction (R1). It is clearly seen in the picture of the IRP for R1 (Figure 2) that despite the larger path from TS to reactant than to product, the TS is structurally closer to reactants than to products. Figure 1 for R1 shows that despite the fact that the H transfer is quite advanced in the TS (d(N−H) = 1.454 Å and d(C−H) = 1.155 Å), the C−N bond length is closer to the reactant than to the product. This indicates that the length of the IRP is not a suitable parameter to characterize the Hammond character of a reaction.

Let us start the discussion on the electronic chemical potential and molecular hardness behavior for the reactions studied by analyzing the μ and η values obtained from eq 8. It is interesting to note that the anti-Hammond reactions following the β_s criterium present η (TS) values that are closer to η in products, in contrast to the Hammond type reactions where the η (TS) are closer to the values of η for the reactant, with the exception of R3 where the TS is the hardest species. Further, in all Hammond reactions analyzed the products are harder than reactants, whereas the reverse is true for anti-Hammond reactions. In all cases, except R2 and R3, the TSs are softer than either the reactants or products, in agreement with the PMH. Although the PMH do not require the most stable species among

TABLE 1: B3LYP/6-31+G*//HF/6-31G* Total Energies (in hartrees), Relative Energies Referred to the Less Stable Isomer for Each Rearrangement Reaction (in kcal mol^{-1}), Orbital Energies (in hartrees), Chemical Potential (in hartrees), Hardness (in hartrees), Length of the IRP from the TS (R_X, in uma$^{1/2}$ bohr), the Structural Proximity Parameter (β_s), and the Brönsted Parameter (β_b)

R1	HNC	TS‡	HCN	R1	HNC	TS‡	HCN
E	−93.403603	−93.351094	−93.426979	η^a	0.1640 (0.2476)	0.1344 (0.2443)	0.1878 (0.2857)
ΔE	0.0	32.9	−14.7	R_X	−4.35	0.00	3.27
ϵ_{HOMO}	−0.3258	−0.3523	−0.3762	β_s		−0.1447	
ϵ_{LUMO}	0.0023	−0.0835	−0.0006	β_b		0.4540	
μ^a	−0.1618 (−0.2000)	−0.2179 (−0.2297)	−0.1884 (−0.2313)				

R2	HClO	TS‡	HOCl	R2	HClO	TS‡	HOCl
E	−535.824123	−535.829309	−535.935721	η^a	0.0598 (0.1576)	0.0616 (0.1617)	0.0783 (0.1887)
ΔE	0.0	−3.3[b]	−70.0	R_X	−4.31	0.00	3.72
ϵ_{HOMO}	−0.2957	−0.3124	−0.3190	β_s		−0.1956	
ϵ_{LUMO}	−0.1761	−0.1891	−0.1625	β_b		0.2932[c]	
μ^a	−0.2359 (−0.2396)	−0.2508 (−0.2537)	−0.2408 (−0.2482)				

R3	HONS	TS‡	HSNO	R3	HONS	TS‡	HSNO
E	−528.669819	−528.626530	−528.679810	η^a	0.0665 (0.1628)	0.0827 (0.1805)	0.0774 (0.1741)
ΔE	0.0	27.2	−6.3	R_X	−2.42	0.00	3.32
ϵ_{HOMO}	−0.2604	−0.2929	−0.2619	β_s		−0.080	
ϵ_{LUMO}	−0.1275	−0.1275	−0.1072	β_b		0.4740	
μ^a	−0.1939 (−0.2008)	−0.2102 (−0.2173)	−0.1846 (−0.1899)				

R4	H_2SO	TS‡	HSOH	R4	H_2SO	TS‡	HSOH
E	−474.537267	−474.474832	−474.576606	η^a	0.1170 (0.1988)	0.0858 (0.1796)	0.1050 (0.1961)
ΔE	0.0	39.2	−24.7	R_X	−2.69	0.00	2.19
ϵ_{HOMO}	−0.2606	−0.2492	−0.2552	β_s		0.7840	
ϵ_{LUMO}	−0.0266	−0.0776	−0.0452	β_b		0.4392	
μ^a	−0.1436 (−0.1692)	−0.1634 (−0.1739)	−0.1502 (−0.1708)				

R5	H_2SeO	TS‡	HSeOH	R5	H_2SeO	TS‡	HSeOH
E	−2475.744805	−2475.684827	−2475.788618	η^a	0.1119 (0.1883)	0.0780 (0.1665)	0.0924 (0.1805)
ΔE	0.0	37.6	−27.5	R_X	−3.03	0.00	2.39
ϵ_{HOMO}	−0.2591	−0.2443	−0.2437	β_s		0.7091	
ϵ_{LUMO}	−0.0352	−0.0883	−0.0588	β_b		0.4318	
μ^a	−0.1471 (−0.1712)	−0.1663 (−0.1748)	−0.1512 (−0.1708)				

R6	F_2S_2	TS‡	FSSF	R6	F_2S_2	TS‡	FSSF
E	−996.020360	−995.954279	−996.028429	η^a	0.0991 (0.1903)	0.0524 (0.1441)	0.1155 (0.2048)
ΔE	0.0	41.5	−5.1	R_X	−7.38	0.00	9.68
ϵ_{HOMO}	−0.2901	−0.2828	−0.3023	β_s		−0.1476	
ϵ_{LUMO}	−0.0918	−0.1781	−0.0712	β_b		0.4855	
μ^a	−0.1910 (−0.1962)	−0.2304 (−0.2309)	−0.1868 (−0.1934)				

R7	H_3PO	TS‡	H_2POH	R7	H_3PO	TS‡	H_2POH
E	−418.364892	−418.265188	−418.370949	η^a	0.1381 (0.2175)	0.0853 (0.1727)	0.1139 (0.1959)
ΔE	0.0	62.6	−3.8	R_X	−4.58	0.00	2.56
ϵ_{HOMO}	−0.2986	−0.2389	−0.2588	β_s		0.0025	
ϵ_{LUMO}	−0.0224	−0.0682	−0.0311	β_b		0.4926	
μ^a	−0.1605 (−0.1881)	−0.1536 (−0.1653)	−0.1450 (−0.1679)				

R8	H_3AsO	TS‡	H_2AsOH	R8	H_3AsO	TS‡	H_2AsOH
E	−2310.741481	−2310.659745	−2310.788363	η^a	0.1192 (0.1892)	0.0802 (0.1637)	0.1141 (0.1928)
ΔE	0.0	51.3	−29.4	R_X	−3.11	0.00	3.14
ϵ_{HOMO}	−0.2776	−0.2376	−0.2669	β_s		0.0400	
ϵ_{LUMO}	−0.0391	−0.0772	−0.0387	β_b		0.4436	
μ^a	−0.1584 (−0.1826)	−0.1574 (−0.1662)	−0.1528 (−0.1758)				

R9	CH_2SH_2	TS‡	CH_3SH	R9	CH_2SH_2	TS‡	CH_3SH
E	−438.585667	−438.544995	−438.700460	η^a	0.0841 (0.1583)	0.0717 (0.1496)	0.1171 (0.1955)
ΔE	0.0	25.5	−72.0	R_X	−5.68	0.00	5.98
ϵ_{HOMO}	−0.1907	−0.2364	−0.2411	β_s		−0.2367	
ϵ_{LUMO}	−0.0225	−0.0930	−0.0070	β_b		0.3285	
μ^a	−0.1066 (−0.1241)	−0.1647 (−0.1830)	−0.1241 (−0.1509)				

[a] In parentheses values calculated using eq 7. [b] The HF/6-31G* value for this energy barrier is 14.2 kcal mol^{-1}. [c] Value computed at the HF/6-31G* level (the B3LYP/6-31+G*//HF/6-31G* result is not available because of the negative value of $\Delta E^{\ddagger}$ obtained at this level of theory).

reactant and product be the hardest, it is interesting to compare their values of η. We note that in the Hammond reactions the hardest species is the most stable one, whereas the anti-Hammond reactions seem to be characterized by a larger

hardness in the reactant. The only exception to this statement is R3, although the differences in hardness among reactant, TS, and product are small.

On the other hand, since in all cases the chemical potential does not remain constant, our results are confirming the fact that the PMH may be satisfied even in cases where the chemical potential and the external potential vary along the reaction coordinate (Hammond type reactions). From our analysis one can state that generally Hammond reactions satisfy the PMH and furthermore, the hardest species among reactants and products corresponds to the most stable one, thus extending the validity of the PMH to the whole energy profile. In contrast to this, the anti-Hammond reactions satisfy the PMH but the hardest species does not necessarily correspond to the most stable one. It is important to point out that in both cases the chemical potential does not remain constant along the reaction coordinate. In most cases, μ is minimal in the TS, showing that the chemical potential profile follows that of the hardness and it is opposite to that of the energy.

It is worth noting that, as already pointed out,[11] the same qualitative conclusions achieved above can also be reached from the μ and η values obtained from eq 7 (given in parentheses in Table 1). The only exception is the anti-Hammond reaction R8, in which the hardest species is the product instead of the reactant, and therefore, the η (TS) is closer to η for the reactant. However, it is also true that in this particular case the difference of η between reactant and product is small.

Another interesting feature that appears in Table 1 concerns the energy of the HOMO, when going from reactant to product, ϵ_H goes down in the Hammond type reactions whereas it goes up in the anti-Hammond reactions. These observations suggest that Hammond reactions might be characterized by higher ionization potentials of the products, and therefore, in these reactions the products will be less reactive in front of an electrophilic attack as compared to the reactants. On the contrary, for the anti-Hammond reactions one could expect that the products will be more reactive in front of electrophiles. Probably the previous knowledge of the relative electrophilicity of reactants and products may help predict the Hammond or anti-Hammond behavior of the reaction where they are involved.

Summary and Conclusions

The Hammond or anti-Hammond behavior of a chemical reaction have been qualitatively characterized through β_b and β_s, the former giving information about the relative location of the TS and the latter giving a measure of similarity of the TS electron density topology to those of reactants and products. We have found that, in general, both Hammond and anti-Hammond reactions satisfy the PMH and in Hammond reactions the PMH can be extended to a global feature along reaction coordinate: among the stationary points the softest species is the TS and the hardest species corresponds to the most stable one. On the other hand, since the Hammond or anti-Hammond behavior seems to be also related to the reactivity characteristics of reactants and products, the study of local reactivity indexes in combination with the present approach should give more insight about the global characterization of a chemical reaction. Finally, it is worth noting that the main goal of this work has been to discuss qualitatively the validity of the HP and the PMH through the use of the β_b and β_s coefficients. To pursue this goal we have used a reasonable level of calculation that certainly it should be improved for quantitative purposes. However, we think that the qualitative conclusions reached by this work should not be altered in a significant way by the use of larger basis sets and higher-level theoretical methods.

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