Characterization of Chemical Reactions from the Profiles of Energy, Chemical Potential, and Hardness

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A theoretical model relating the kinetic, mechanistic, and thermodynamics aspects of a chemical reaction is presented. The model is based upon the consistency between the principle of maximum hardness and the Hammond postulate, and it is used to obtain insights about the reaction mechanisms and to define rate constants in terms of the chemical potential and hardness of activation. An important result is that when both electronic properties are allowed to vary along the reaction coordinate, it is found that the activation process is controlled by the change in chemical potential while the relaxation one is controlled by the change in hardness.

1. Introduction

A chemical reaction can be seen as resulting from redistribution of electron density among atoms in a molecule, even in cases where the total number of electrons is conserved along the reaction coordinate. Density functional theory (DFT) is quite well suited to describe such electronic reorganization processes; it provides the theoretical basis for concepts like electronic chemical potential (μ) and molecular hardness (η). The former property characterizes the escaping tendency of electrons from the equilibrium system, while η can be seen as a resistance to charge transfer.[1−6] Both are global properties and are implicated in the reactivity of molecular systems. The study of their profiles along a reaction coordinate has been shown to be useful to rationalize different aspects of the progress of chemical reactions.[7−10]

Formal definitions of μ and η were given by Parr et al,[1] and Parr and Pearson,[2] respectively. A three-points finite difference approximation leads to working formulas of these quantities in terms of the vertical ionization potential and electron affinity of the neutral molecule. The Koopmans theorem can also be used to write μ and η in terms of the energy of frontier molecular orbitals.[5] Chemical potential and hardness are very well established quantities that have evoked considerable research activity in the last years.[7−13]

One major focus of attention in DFT is the principle of maximum hardness (PMH) that asserts that molecular systems at equilibrium tend to states of high hardness.[4,11−13] There are many examples showing that the PMH complements the minimum energy criterion for stability. We have shown in recent papers that the PMH can also be helpful in identifying transition states (TS) since they must present minimum values of hardness.[9] Rationalizing the transition state through the PMH leads to establishing a bridge connecting electronic and energetic properties, *i.e.,* reaction mechanisms and thermodynamics. This is of considerable theoretical interest since it complements the well-known relationships between kinetics and thermodynamics.[14]

There are many relationships connecting kinetics and thermodynamics, most of them providing important predictive tools to rationalize chemical reactions. Since the initial proposal that properties of the transition state should reflect in part those of reactants and product,[15−18] much work has been done about the rate-equilibrium concept and the application of linear free energy relationships. In particular, very useful approaches and empirical rules to characterize the transition state have been proposed. Among them, the Hammond postulate[18] is certainly the most important tool to obtain insights on the structure and properties of TSs from the knowledge of the structure and properties of reactants and products species.

In this paper an approach that connects electronic, kinetic, and thermodynamic properties of chemical reactions is presented. We will deal with the chemical potential and molecular hardness as electronic properties, the activation energy as a kinetic property, and the reaction energy as a thermodynamic property. The PMH in connection with the Hammond postulate provides the necessary elements to achieve this goal.

2. Theory

2.1. General Definitions. We consider a chemical reaction of the type $\mathbf{R} \rightarrow (\mathrm{TS})^{\ddagger} \rightarrow \mathbf{P}$, where the reactants change into products passing by a transition state. We assume that these states are connected through a reduced reaction coordinate ω that measures the reaction progress when going from reactants to products, ω goes from 0 (**R**) to 1 (**P**) passing by an intermediate value $\omega = \beta$ at the transition state. It is always possible to find a scaling procedure to express ω in terms of the actual reaction coordinate.[10] In Figure 1a we display the classical picture of a chemical reaction represented by its energy profile along the reaction coordinate, and in Figure 1b we show the energy profile of the same chemical reaction but now along the reduced variable ω. It should be noted that the main interest of working in the ω representation is that it provides a correct and straightforward characterization of the position and the energy of the transition state, this allowing a qualitative rationalization of the chemical process.

We have shown previously that a function representing the relative reaction potential energy can be written as:[8−10,19,20]

$$V(\omega) = V(0) + K_V f(\omega) + \omega \Delta V^\circ \qquad (1)$$

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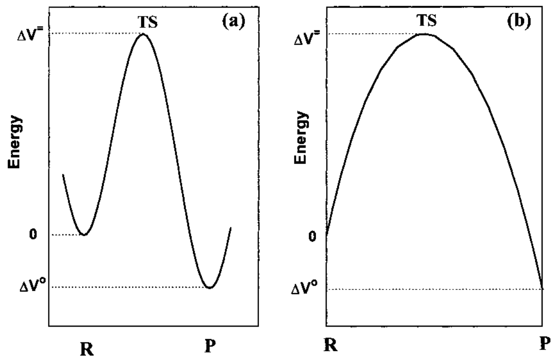

Figure 1. Qualitative sketch of the evolution of the potential energy along the reaction coordinate (a) and following the reduced reaction coordinate (b).

where $V(0)$ is the reference energy, $K_V > 0$ is a parameter that, as we shall see, is an intrinsic property of the reaction, and $\Delta V° = [V(1) - V(0)]$ is the overall reaction energy. $f(\omega)$ is a function that must be symmetric about $\omega = {}^1/_2$, where it must be maximal. Many conveniently normalized functions qualify with this requirement; they all must have the same behavior about $\omega = {}^1/_2$ and therefore they only may differ in their wings. The function $f(\omega) = \omega(1 - \omega)$ is probably one of the simplest functions satisfying the above boundary condition, and it has been already used to represent different types of chemical process.[8−10] We shall see that besides fulfilling the mathematical requirements $f(\omega)$ satisfies the physical consistency of our theoretical model.

Since μ and η are global properties of the system, their evolution along ω can be expressed through the same analytic form already used for $V(\omega)$ in eq 1. Therefore we have for the chemical potential[10]

$$\mu(\omega) = \mu(0) + K_\mu f(\omega) + \omega\Delta\mu° \tag{2}$$

and similarly for the molecular hardness[10]

$$\eta(\omega) = \eta(0) + K_\eta f(\omega) + \omega\Delta\eta° \tag{3}$$

The sets of parameters ($\Delta\mu°$, K_μ) and ($\Delta\eta°$, K_μ) have the same meaning that ($\Delta V°$, K_V) have for $V(\omega)$. Note that $V(\omega)$, $\mu(\omega)$, and $\eta(\omega)$ are relative to their values at $\omega = 0$ and for simplicity we shall use the following notation: $\Delta P(\omega) = P(\omega) - P(0)$, $P = V, \mu, \eta$.

2.2. Relations between μ, η, and V. It is clear from the above equations that V, μ, and η are connected through $f(\omega)$. To obtain an expression relating the energy with the chemical potential, we combine eqs 1 and 2:

$$\Delta V_\eta(\omega) = \omega\Delta V° + Q_\eta[\Delta\mu(\omega) - \omega\Delta\mu°] \tag{4}$$

This can be seen as the reaction potential energy for processes where hardness remains constant along the reaction coordinate. Similarly, combination of eqs 1 and 3 leads to an expression for the energy in which the chemical potential is constant along ω:

$$\Delta V_\mu(\omega) = \omega\Delta V° + Q_\mu[\Delta\eta(\omega) - \omega\Delta\eta°] \tag{5}$$

Finally, combination of eqs 2 and 3 leads to[10]

$$\Delta\mu(\omega) = \omega\Delta\mu° + Q[\Delta\eta(\omega) - \omega\Delta\eta°] \tag{6}$$

The new parameters $\{Q_\eta, Q_\mu, Q\}$ are related to the old ones ($\{K_V, K_\mu, K_\eta\}$) through $Q_\eta = K_V/K_\mu$ and $Q_\mu = K_V/K_\eta$; in addition $Q = Q_\mu/Q_\eta$. It has been shown that these new parameters are related to the electronic charge redistributed during the chemical reaction.[10] From the above equations it is possible to obtain a global expression accounting for the simultaneous evolution of the three properties along a reaction coordinate, combination of eqs 4 and 5 yields

$$\begin{aligned}\Delta V(\omega) &\equiv \frac{1}{2}[\Delta V_\eta(\omega) + \Delta V_\mu(\omega)] \\ &= \omega\Delta V° + \frac{1}{2}Q_\eta[\Delta\mu(\omega) - \omega\Delta\mu°] + \frac{1}{2}Q_\mu[\Delta\eta(\omega) - \omega\Delta\eta°]\end{aligned} \tag{7}$$

It is worthwhile to stress the fact that the above equation combines the reaction potential energy with the mechanistics aspects of the chemical reaction, the latter are included in the electronic properties μ and η. Therefore, the reaction potential energy along ω is due to the rearrangement of the electron density expressed through the changes in μ and η. On the other hand, the explicit dependence on the reaction coordinate ensures that the change in the external potential is implicitly considered through systematic geometry relaxation along ω.

2.3. Hammond Postulate (HP). Having the analytic form for the reaction potential, the position of the transition state at $\omega = \beta$ is determined by direct differentiation of $V(\omega)$:

$$\left(\frac{dV}{d\omega}\right)_{\omega=\beta} = 0 \Rightarrow \beta = \frac{1}{2} + \frac{\Delta V°}{2K_V} \tag{8}$$

The parameter β is a measure of the degree of resemblance of the transition state to the product(s), an index quantifying the proposal of Leffler[17] in that properties of the transition state should reflect in part those of reactants and products. In connection with this, in 1953, G. S. Hammond postulated that in an exothermic reaction the transition state will be likely to resemble the reactants while in an endothermic reaction it will resemble the products.[18] The Hammond postulate is a central concept in chemistry because it provides a connection between the kinetics and thermodynamics of chemical reactions.

It is important to mention that proper thermodynamic discussion should be addressed in terms of free energies at finite temperature. However, since for macroscopic systems at the 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 discussion concerning thermodynamics and chemical kinetics.[5]

A major corollary of our definition of β (eq 8) is that it can be considered as an index quantifying the HP: the transition state is located closer to the product ($\beta > {}^1/_2$) for endothermic reactions ($\Delta V° > 0$) and closer to the reactants ($\beta < {}^1/_2$) for exothermic reactions ($\Delta V° < 0$). Since the barrier position is difficult to locate experimentally, the HP continues to be an attractive tool that has been used to characterize the structure and nature of the transition state.[9,10,21−24] It should be mentioned that eq 8 is consistent with the Leffler equation for rate−equilibrium relationships in which β was defined as the Brønsted coefficient and obtained from the activation energy.[17] We shall see in section 2.7 how these quantities are related.

2.4. Principle of Maximum Hardness (PMH). The principle of maximum hardness asserts that molecular systems at equilibrium tend to states of high hardness; transition states should therefore present minimum values of hardness. It has been shown that the PMH holds under the constraints that the external potential and the electronic chemical potential must remain constant upon distortion of the molecular structure,[25] although it seems to be valid even under less severe conditions than the ones stated above.[8−10,26−28] Within our framework, a necessary condition for the PMH to hold is that the curvatures of $V(\omega)$ and $\eta(\omega)$ be opposite, and therefore, differentiating eq 5, the reaction potential at constant μ, we obtain

$$\left(\frac{d^2V_\mu}{d\omega^2}\right) = Q_\mu \left(\frac{d^2\eta}{d\omega^2}\right) \tag{9}$$

The opposite curvature condition leads to a negative Q_μ. The condition $Q_\mu < 0$ is an important qualitative result that will be used in the search of consistency between the PMH and the HP.

2.5. Consistency between the HP and the PMH. As already mentioned, the PMH has been demonstrated under the condition that the chemical potential remains constant along the reaction coordinate; furthermore, there is evidence showing that in most cases the variation of chemical potential is small, so we use eq 5 to obtain rules for consistency between the PMH and the HP.[9] The condition for a critical point in eq 5 leads to

$$\left(\frac{dV_\mu}{d\omega}\right)_\beta = \Delta V^\circ + Q_\mu \left[\left(\frac{d\eta}{d\omega}\right)_\beta - \Delta\eta^\circ\right] = 0 \tag{10}$$

The PMH asserts that

$$\left(\frac{dV_\mu}{d\omega}\right)_\beta \approx \left(\frac{d\eta}{d\omega}\right)_\beta = 0 \tag{11}$$

yielding the following relation between the energy of the reaction and the change of hardness:

$$\Delta V^\circ = Q_\mu \Delta\eta^\circ \tag{12}$$

This shows that the change of hardness between reactants and products provides fundamental insight for the description of the thermodynamic aspect of a chemical reaction. Note that the reaction energy ΔV° makes the bridge between the hardness and the Brønsted coefficient β through the Hammond postulate, eq 8. Now, from the PMH $Q_\mu < 0$, and therefore, eq 12 in consistency with the HP allows one to characterize qualitatively reactants and products in terms of their relative molecular hardness:

1. Endothermic Reactions:

$$\Delta V^\circ > 0 \Rightarrow \beta > \frac{1}{2} \Rightarrow \Delta\eta^\circ < 0 \Rightarrow \eta_R > \eta_P \tag{13}$$

2. Exothermic Reactions:

$$\Delta V^\circ < 0 \Rightarrow \beta < \frac{1}{2} \Rightarrow \Delta\eta^\circ > 0 \Rightarrow \eta_R < \eta_P \tag{14}$$

3. Isoenergetic Reactions:

$$\Delta V^\circ = 0 \Rightarrow \beta = \frac{1}{2} \Rightarrow \Delta\eta^\circ = 0 \Rightarrow \eta_R = \eta_P \tag{15}$$

Note that following the sign of ΔV°, the reactions tend to go in the direction that produces the hardest species. This is a very important result that is not a simple consequence of the PMH. In fact, the maximum of the PMH is a local one only; therefore, η should increase in going from the TS to either **R** or **P**, but there is no requirement that the most stable species be the hardest. Therefore, chemical reactions tend to go in the direction that produces the hardest species as a result of the combination of the HP and the PMH. This rule was first formulated by Datta,[29] elaborated further by Hati and Datta,[30] and more recently derived from the analysis of the electronic activation energy and the bond energy in exchange reactions by Gázquez.[31]

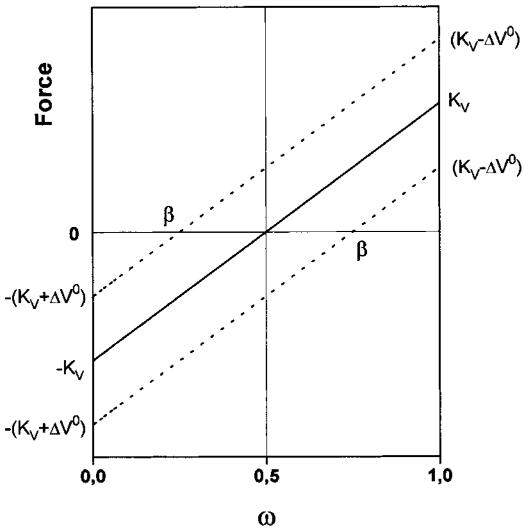

Figure 2. Driving force of the chemical reaction along the reaction coordinate. The reference line (solid) represents an isoenergetic reaction. The upper and lower lines (dashed) represent exoenergetic and endoenergetic reactions, respectively.

2.6. Reaction Mechanisms. To put the concept of reaction mechanism on a quantitative basis we proceed as follows. Let the force acting on the system to bring reactants into products depend only on the position along the reaction coordinate. Such a force is then defined as

$$F(\omega) = -\frac{dV}{d\omega} \tag{16}$$

and from eq 1 we obtain

$$F(\omega) = -(K_V + \Delta V^\circ) + (2K_V)\omega \tag{17}$$

In Figure 2 we display the qualitative behavior of the force along ω for different types of reactions. We note that the force is negative in the interval $0 \le \omega < \beta$ (the reactants region) and it is positive in the products region ($\beta < \omega \le 1$). To have an adequate description of the whole chemical reaction, it is useful to distinguish the different processes taking place along the reaction coordinate. Within the reactants region an activation process is taking place, whereas in the product region we have a relaxation process; the work associated with these processes is defined by

$$W_{act} = \int_0^\beta F(\omega)\, d\omega \qquad W_{rel} = \int_\beta^1 F(\omega)\, d\omega \tag{18}$$

Isoenergetic reactions present the transition state at $\beta = {}^1/_2$, here the amount of activation work is equal to that of relaxation work. Therefore, amount of energy required for the activation becomes equal to the amount of energy released during relaxation. In contrast to this, exoenergetic reactions are characterized by an early transition state ($\beta < 1/2$) and the amount of activation work is smaller than the amount of relaxation work. Finally, an endoenergetic reaction is characterized through a $\beta > {}^1/_2$ and an amount of activation work larger than that of relaxation work.

In the following paragraphs we shall see that the activation and relaxation processes are related to chemical potential and hardness driven processes. The use of eq 7 instead of eq 1 to define $F(\omega)$ leads to

$$F(\omega) = -\left[\Delta V^\circ + \frac{1}{2}Q_\eta\left(\frac{d\mu}{d\omega} - \Delta\mu^\circ\right) + \frac{1}{2}Q_\mu\left(\frac{d\eta}{d\omega} - \Delta\eta^\circ\right)\right] \tag{19}$$

where further reductions are possible if we use eqs 2 and 3 for the derivatives of μ and η. The transition state condition on eq 7 leads to

$$\Delta V^\circ = \frac{1}{2}(Q_\eta\Delta\mu^\circ + Q_\mu\Delta\eta^\circ) \tag{20}$$

This is so because it has been shown that at the transition state μ and η pass through or very near to a critical point and therefore $(dV/d\omega)_{TS} = 0$ and $(d\mu/d\omega)_{TS} = (d\eta/d\omega)_{TS} \approx 0$. The above condition on the reaction energy allows one to rewrite eq 7 as

$$\Delta V(\omega) = \frac{1}{2}Q_\eta\Delta\mu(\omega) + \frac{1}{2}Q_\mu\Delta\eta(\omega) \tag{21}$$

Therefore, for all ω there is a unique expression accounting for the μ and η dependence of V. Consequently, the force appears to be split into two contributions that are associated with chemical potential and hardness driving processes:

$$F(\omega) = -\frac{1}{2}Q_\eta\frac{d\mu}{d\omega} - \frac{1}{2}Q_\mu\frac{d\eta}{d\omega} \tag{22}$$

This equation together with Figure 2 permit one to analyze $F(\omega)$-in terms of the sign that it takes when moving along ω:

$$F(\omega) < 0 \Longrightarrow Q_\eta\frac{d\mu}{d\omega} > |Q_\mu|\,\frac{d\mu}{d\omega} \qquad (0 \le \omega < \beta) \tag{23}$$

And when going from the reactants to the transition state (the activation process), it is the chemical potential that drives the reaction. At the transition state we have

$$F(\omega) = 0 \Longrightarrow Q_\eta\frac{d\mu}{d\omega} = |Q_\mu|\,\frac{d\eta}{d\omega} \qquad (\omega = \beta) \tag{24}$$

and both driving forces are equilibrated and cancel each other. When stepping down from the transition state to the products (the relaxation process), we have

$$F(\omega) > 0 \Longrightarrow Q_\eta\frac{d\mu}{d\omega} < |Q_\mu|\,\frac{d\eta}{d\omega} \qquad (\beta < \omega \le 1) \tag{25}$$

and this part of the reaction is controlled by the hardness term as the system rearranges itself to reach a maximum hardness configuration. In summary, activation processes are basically driven by the chemical potential, whereas relaxation processes are driven by the change in hardness.

It is important to note that since the reaction coordinate can be expressed in terms of changes in the internal coordinates of atoms in the molecules, $F(\omega)$ can be expressed as a sum of local contributions. This fact can be used to identify the specific local interactions that are responsible for the activation and relaxation processes. Furthermore, the change of the internal coordinates will produce a change in the electronic external potential $v(\vec{r})$ and therefore it should be possible to characterize $F(\omega)$ from eq 22 in terms of $[\delta\mu/\delta v(\vec{r})]_N$ and $[\delta\eta/\delta v(\vec{r})]_N$, which may lead to new local reactivity rules.

2.7. Transition State. Putting β in eq 1 yields the following expression for the energy of the transition state:

$$V(\beta) = \left[\frac{1}{4}K_V + \frac{1}{2}\Delta V^\circ + \frac{(\Delta V^\circ)^2}{4K_V}\right] \equiv \Delta V^\ddagger \tag{26}$$

$\Delta V^\ddagger$ is the potential energy barrier or activation energy. From the above expression for $\Delta V^\ddagger$ we obtain an alternative definition for the Brønsted coefficient that is consistent with eq 8 and that corresponds to the original definition obtained by Leffler from the rate−equilibrium relationships:[17]

$$\beta = \frac{\partial\Delta V^\ddagger}{\partial\Delta V^\circ} \tag{27}$$

Consistency between the mathematical definition of β given in eq 8 and determined by the analytic form of the reaction potential $V(\omega)$ with the physical characterization of eq 27 determined from the rate−equilibrium relationships shows the correctness of the analytic form we use for the reaction potential.

The evaluation of eq 7 in $\omega = \beta$ and the use of eq 20 lead to an alternative expression for the activation energy but now in terms of the activation chemical potential $[\Delta\mu^\ddagger \equiv \Delta\mu(\beta)]$ and the activation hardness $[\Delta\eta^\ddagger \equiv \Delta\eta(\beta)]$:

$$\Delta V^\ddagger = \frac{1}{2}Q_\eta\Delta\mu^\ddagger + \frac{1}{2}Q_\mu\Delta\eta^\ddagger \tag{28}$$

This equation connecting the three activation properties provides new interpretations of the nature of activation energies; it tells us that the activation energy is basically an electronic property of the transition state, and characterization of the TS electron density should provide the elements to advance the reaction mechanisms in terms of specific local interactions that can be identified through the use of DFT-based reactivity indexes.

On the other hand, if we assume that the chemical potential remains constant along the reaction coordinate, then to determine $\Delta\mu^\ddagger$, we have to use eq 5, instead of eq 7, under the condition given in eq 12. This leads to

$$\Delta V^\ddagger = Q_\mu\Delta\eta^\ddagger \tag{29}$$

Since $\Delta V^\ddagger > 0$ and $Q_\mu < 0$, then $\Delta\eta^\ddagger < 0$. As a qualitative result, we obtain $\eta(TS) < \eta(R)$. The hardness at the transition state is smaller than that of the reactants, as expected from the PMH that asserts that molecules tend to a maximum hardness configuration.

2.8. Kinetic Aspects. Application of the above ideas to determine rate constants is quite straightforward. Assuming an Arrhenius model[32] for the rate constant of a process with activation energy $\Delta V^\ddagger$, we write

$$k = Ae^{-\Delta V^\ddagger/RT} \tag{30}$$

where A is the Arrhenius factor, R is the gas constant, and T is the temperature. With the aim of finding an electronic interpretation of the rate constant, we use eq 28 to put k in terms of the finite temperature activation chemical potential and hardness:

$$k = Ae^{-Q_\eta\Delta_\mu{}^\ddagger/2RT}e^{-Q_\mu\Delta_\eta{}^\ddagger/2RT} \tag{31}$$

Consistent with what we expressed in section 2.6, we now define the activation and relaxation rate constants as

$$k_{act} = Ae^{-Q_\eta\Delta_\mu{}^\ddagger/RT} \tag{32}$$

$$k_{rel} = Ae^{-Q_\mu\Delta_\eta{}^\ddagger/RT} \tag{33}$$

This leads to an overall rate constant expressed as the geometrical mean of the two processes:

$$k = \sqrt{k_{act}k_{rel}} \tag{34}$$

A chemical reaction can be seen as a two-step process. First, there is an activation step that is controlled by the change in the chemical potential; it should be associated with a charge transfer. Then there is a reshuffling of the charge distribution, the relaxation process from the transition state to a new (or to the old) equilibrium position. In the relaxation step the maximum hardness principle applies. This picture of a chemical reaction is consistent with the first proof of the HSAB principle[33] given by Chattaraj et al:[34] when acid A and base B interact to give AB, there is first a charge transfer, controlled by μ, and then there is a reshuffling of the charge distributions, which is controlled by η.

2.9. General μ and η Dependence of V. Equation 20 shows that for all ω there is a unique expression for the μ and η dependence of V. Moreover and in close connection with this, we have shown that the parameters Q_η, and Q_μ are the slopes associated with the differential expression for $V(\mu,\eta)$[10]

$$\begin{aligned} dV &= \left(\frac{\partial V}{\partial \mu}\right)_\eta d\mu + \left(\frac{\partial V}{\partial \eta}\right)_\mu d\eta \\ &= \frac{1}{2}Q_\eta d\mu + \frac{1}{2}Q_\mu d\eta \end{aligned} \tag{35}$$

The slopes can be determined by combining eqs 4−6, or simply from eqs 20 and 28:

$$Q_\eta = \frac{(\Delta V^\ddagger - \Delta V^\circ)}{(\Delta \mu^\ddagger - \Delta \mu^\circ)} \tag{36}$$

and

$$Q_\mu = \frac{(\Delta V^\ddagger - \Delta V^\circ)}{(\Delta \eta^\ddagger - \Delta \eta^\circ)} \tag{37}$$

We have mentioned that these parameters together with

$$Q = \frac{Q_\mu}{Q_\eta} = \frac{(\Delta \mu^\ddagger - \Delta \mu^\circ)}{(\Delta \eta^\ddagger - \Delta \eta^\circ)} \tag{38}$$

are related to the charge redistributed during the chemical reaction.[10] Even though recently we have obtained formal definitions for Q_η and Q_μ in terms of N, μ, η, and γ[35] (N being the total number of electrons and $\gamma = (\partial\eta/\partial N)_v$[36]), more work should be done for a precise identification of these parameters on each particular case. Qualitatively, it can be noted that since, in general, μ presents smaller variation along ω than η, $|Q_\eta| > |Q_\mu|$ and since $\Delta V^\ddagger > 0$ and $\Delta\eta^\ddagger > 0$, then $Q_\mu < 0$, as already established in eq 9.

On the other hand, it should be mentioned that the numerical determination of Q_η and Q_μ is quite direct from theoretical calculations since reactants, products, and transition states are usually well characterized. From the experimental viewpoint, the activation properties are more difficult to obtain, although they can be determined from rate experiments at various temperatures and using the equation suggested in this paper. Once the parameters are known, it is possible to characterize the trajectory that follows the reaction in the $\{\mu, \eta, V\}$ space, as shown in previous papers.[8−10]

3. Summary and Concluding Remarks

Based upon the search for consistency between the principle of maximum hardness and the Hammond postulate, a theoretical model relating kinetic, mechanistic, and thermodynamics aspects of chemical processes has been proposed. A number of useful formulas to rationalize chemical reactions in terms of the change of the relevant properties along the reaction coordinate have been derived and used for understanding the qualitative behavior of processes having different values for the reaction energy.

Classical concepts were revisited and revalidated through their consistency with new DFT ideas. An important result of this study is that in a chemical reaction the uphill process is controlled by the change in the chemical potential while the downhill one is controlled by the change in the chemical hardness.

Finally, it is worthwhile to mention that few of the relationships that have been qualitatively discussed in this paper have been applied with success in the quantitative rationalization of different kinds of chemical reactions.[8−10,19,20] However, further applications are still necessary, especially to determine the range of validity of the analytic model defining $V(\omega)$, $\mu(\omega)$, and $\eta(\omega)$.

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