J. Phys. Chem. A **2000,** *104,* 11589−11592

Characterization of Elementary Chemical Reactions from Bifurcation Theory

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Received: February 3, 2000; In Final Form: July 25, 2000

A theoretical formalism based upon simple bifurcation theory aimed at rationalizing elementary chemical processes is presented. The study of a generic potential representing the evolution from reactants to products leads us to determine a local bifurcation condition on the parameter space. Our formalism leads us to define topological regions where chemical processes can be analyzed within the Hammond postulate and the principle of maximum hardness framework. Furthermore, if a Gibbs-like potential is assumed to represent the profile of any global property (energy, hardness, and chemical potential) along the reaction coordinate, then a canonical bifurcation which is isomorphous to the *fold* catastrophe is obtained.

1. Introduction

A chemical reaction can be seen as resulting from reorganization and redistribution of electron density among atoms in the molecules. It has been shown that density functional theory (DFT) is quite well suited to describe such electronic reorganization processes through concepts such as electronic chemical potential (μ) and molecular hardness (η), which are implicated in the reactivity of chemical species.[1] μ characterizes the escaping tendency of electrons from the equilibrium system,[2] while η can be seen as a resistance to charge transfer.[3] Numerical determination of μ and η is possible through working formulas based upon the finite-difference approximation that can be found elsewhere.[1] The chemical potential and hardness, global properties of the system, are by now very well-established quantities, and they have induced considerable research activity in the last few years.[4−8] Furthermore, the study of the profiles of μ and η along a reaction coordinate and their connection with the energy profile has been shown to be useful in rationalizing rate and thermodynamic aspects of chemical reactions.[7]

The Hammond postulate (HP)[9] and the principle of maximum hardness (PMH)[4,5] have been invoked as powerful tools for a qualitative characterization of transition states (TSs).[7,8] The HP interrelates the position of the TS with the exo- and endothermicity of the reaction. Accordingly, the TS for endothermic reactions will be closer to the products (P), and for exothermic reactions it will be closer to the reactants (R). On the other hand, the PMH asserts that molecular systems at equilibrium tend to states of high hardness; a corollary of this principle is that the TS must present a minimum value for the hardness.[6−8] It has been shown that consistency between the HP and the PMH leads to establishment of a bridge connecting electronic and energetic properties, i.e., reaction mechanisms and thermodynamics.[7] This is of considerable theoretical interest since it complements the well-known relationships between kinetics and thermodynamics.[7] It is thus clear that the theory of chemical reactivity basically relies on the knowledge of the geometrical structures and properties associated with the three stationary states on the potential energy hypersurface. A major focus of attention is therefore a reliable characterization of the TS.[7,8] In this paper we investigate the bifurcations occurring during a chemical reaction to provide new elements that may be used to classify chemical reactions and may help to better characterize the TS. The procedure, based upon simple bifurcation theory, is applied to the study of the internal rotation of glyoxal and its chlorine derivatives.

2. Theoretical Background

2.1. Energy, Chemical Potential, and Hardness. According to Leffler,[10] the derivative of the activation energy ($\Delta V^{\ddagger}$) with respect to the reaction energy (ΔV°) determines the slope β, the Brønsted coefficient, that measures the relative resemblance of the transition state to the product:

$$\beta = \frac{\partial \Delta V^{\ddagger}}{\partial \Delta V^{\circ}} \tag{1}$$

Let us consider an elementary chemical reaction of the type R → TS → P, where the reaction coordinate connects the reactants and the products through the transition state. Reaction path computations allow one to verify that a given transition structure actually links the initial and final structures that are already known. Once this fact is confirmed, the chemical reaction can be studied in *conformational space*, where reactants and products are connected through a reduced reaction coordinate (ω) measuring the reaction progress on going from reactants ($\omega = 0$) to products ($\omega = 1$), passing through the TS ($\omega = \beta$).[7]

A quantitative characterization of the TS of a chemical reaction can be obtained from the following expression for the activation energy:[6−8]

$$\Delta V^{\ddagger} = \frac{1}{4}(k_R + k_P) + \frac{1}{2}\Delta V^{\circ} + \frac{(\Delta V^{\circ})^2}{4(k_R + k_P)} \tag{2}$$

where k_R and k_P are the force constants associated with the reactant and product potential wells. The activation energy of eq 2 is consistent with a quadratic function representing the

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10.1021/jp0004415 CCC: $19.00 © 2000 American Chemical Society
Published on Web 11/17/2000

energy along the reaction coordinate; therefore, it can be seen as an approximation of the actual activation energy. However, it has been shown that it gives quite good estimates of this property in different kinds of chemical reactions.[6−8] On the other hand, it is important to note that eq 2 has the same form of the Marcus equation, originally proposed to characterize electron-transfer processes,[11] and later on used for the interpretation of different kinds of chemical reactions.[6,8,12] Therefore, from eqs 1 and 2 we obtain

$$\beta = \frac{1}{2} + \frac{\Delta V^\circ}{2(k_R + k_P)} \tag{3}$$

The coefficient β quantifies the HP leading to an early TS for exoenergetic reactions ($\Delta V^\circ < 0$, $\beta < 1/2$) and to a later TS for endoenergetic reactions ($\Delta V^\circ > 0$, $\beta < 1/2$). Note that since β depends on the reaction energy only (it depends parametrically on $k_R + k_P$), it is a coefficient that gives the location of 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.[8] The PMH is in turn a local principle in that it does not require the most stable species between reactants and products be the hardest one, although in reactions satisfying the HP this seems to be true.[8] Along the reduced reaction coordinate ω relying on reactants and products, we write the potential energy profile in terms of the μ and η profiles as[6,7]

$$V(\omega) = \omega\Delta V^\circ + {}^1/_2 Q_\eta[\mu(\omega) - \omega\Delta\mu^\circ] + {}^1/_2 Q_\mu[\eta(\omega) - \omega\Delta\eta^\circ] \tag{4}$$

where:

$$Q_\eta = \frac{\Delta V^\ddagger - \Delta V^\circ}{\Delta\mu^\ddagger - \Delta\mu^\circ} \tag{5}$$

and

$$Q_\mu = \frac{\Delta V^\ddagger - \Delta V^\circ}{\Delta\eta^\ddagger - \Delta\eta^\circ} \tag{6}$$

are parameters related to the electronic charge redistributed during the chemical reaction.[6−8] The validity of the PMH entails an opposite curvature for the energy and hardness. This leads to a negative Q_μ.[7]

At this point we have a simple analytic framework to study chemical reactions in terms of $\Delta V^\ddagger$, β, and the relation between energy and the electronic properties, which together with the HP and the PMH were used to classify different types of reactions.[8] It should be stressed that eqs 2 and 3 are consistent with a quadratic analytic form used to represent the evolution of the energy along ω. Most chemical reactions can be rationalized using this simple formalism. However, there are chemical processes that are difficult to classify within this scheme basically because they present anomalous behavior, anti-HP or anti-PMH processes.[8] In such cases, we expect that the use of higher order polynomial functions representing the evolution from reactants to products of $V[\omega]$, $\mu[\omega]$, and $\eta[\omega]$ will produce more general results that may explain peculiar features. Notice that HP and PMH reactions can be explained using eq 3 whereas peculiar chemical processes which do not belong to the above kind of reactions may be classified and characterized differently according to, for example, the pattern of the electronic distribution through topological similarity parameters,[8] or their bifurcation features. This is the way we will explore reactions in this paper.

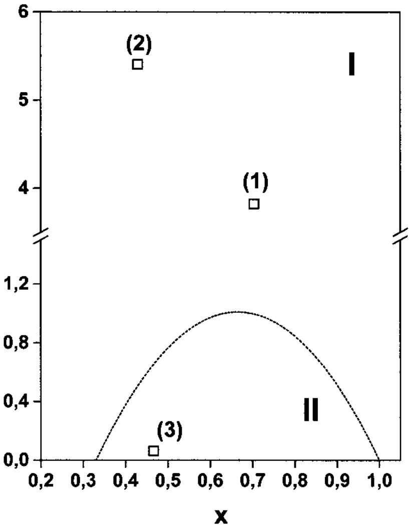

Figure 1. Bifurcation condition (dashed line) partitioning the parameter space in two regions, I and II. The values of y^2 for the rotational isomerization process trans $\rightleftharpoons$ cis of the following molecules have been calculated: (**1**) glyoxal, (**2**) Cl-glyoxal, and (**3**) oxalyl-Cl.

2.2. Elements of Bifurcation Theory. We have shown previously that the evolution of any global property (such as μ, η, or V) along the reduced reaction coordinate ω can be written in terms of a general function (that comes from a cosine Fourier expansion up to the third term[13]) as follows:[6,7]

$$F[\omega] = (A + B)\omega - [A + 3(B - C)]\omega^2 + 2(B - C)\omega^3 \tag{7}$$

where A, B, and C are parameters which are intrinsic properties of the reaction. These parameters are expressed in terms of physical properties associated with reactants and products, that is, the curvature of local minima of V, μ, and η, and the overall change of these properties. Thus, for example, for the energy profile $V[\omega]$, we have $A \equiv k_R + k_P$, $B \equiv k_R - k_P$, and $C \equiv \Delta V^\circ$. Similar expressions for the parameters of the hardness and chemical potential profiles, $\eta[\omega]$ and $\mu[\omega]$, can be found elsewhere.[6] The bifurcation (BF) condition (issued from eliminating the variable ω in the first and second derivatives of F with respect to ω set to zero, that is, $F'[\omega] = F''[\omega] = 0$) leads to

$$y^2 = -9(x - 1)(x - {}^1/_3) > 0 \tag{8}$$

where $x = C/B$, $y = A/B$, and $x \in [{}^1/_3, 1]$. This local condition (8) is a parabola which is plotted by a dashed line in Figure 1. This separatrix makes a partitioning of the (x, y) parameter space in two regions (I and II) where $F[\omega]$ has to display different topologies. In region I falls any chemical reaction, independent of its HP or PMH behavior. In region II lie chemical processes that cannot be viewed as typical chemical reactions in the sense that reactants and/or products may not be clearly identified as stable species. The critical points, ω_c, on each region are located at

$$\omega_c^{\ \mathrm{I}} \approx \frac{1}{2} + \frac{3}{4A}\left(C - \frac{B}{3}\right) \tag{9}$$

$$\omega_c^{\ \mathrm{BF}} = \frac{1}{2} + \frac{A}{6(B - C)} = \frac{1}{2} + \frac{y}{6(1 - x)} \tag{10}$$

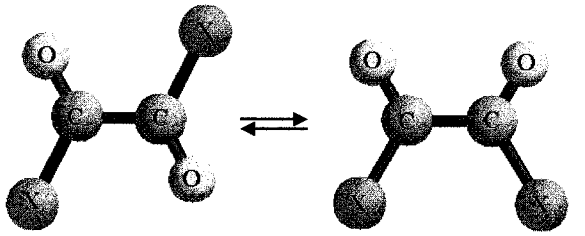

Figure 2. Trans $\rightleftharpoons$ cis isomerization process in glyoxal and chlorine derivatives (X = H, Cl). The torsional angle is defined as the rotation about the CC central bond.

with $-3(B - C) \leq A \leq 3(B - C)$ and

$$\omega_c^{\mathrm{II}} = \frac{1}{2} + \frac{A}{3(B - C)} \mp \left(\frac{A^2}{9(B - C)^2} - \frac{3C - B}{3(B - C)}\right)^{1/2} \qquad (11)$$

Notice that the critical points depend on the three parameters and in all three cases are different from the Brønsted coefficient that in terms of the parameters A, B, and C is given by

$$\beta = \frac{1}{2} + \frac{C}{2A}$$

Comparison between each ω_c and the Brønsted coefficient is not straightforward since the latter index has been defined from a quadratic function representing the energy along ω, the Hammond condition being stated under that definition.[13] In region I the reactant- or product-like character of the reaction should be determined from the index ω_c instead of β. It is important to stress that this new index depends on all three parameters involved in eq 7. Moreover, in contrast to β, which depends on $A = (k_R + k_P)$ and $C = \Delta V°$, ω_c also depends on $B = (k_R - k_P)$, which gives the relative curvature of the potential wells associated with reactants and products. This shows that the reactant- or product-like character of the reaction depends not only on the energy criterion, as originally stated,[9] but also on the relative difference of force constants. Therefore, besides the usual HP behavior, our model gives evidence that it should be possible to find endothermic reactions with a reactant-like TS and exothermic reactions presenting a product-like TS. This is exactly what we have called anti-HP behavior.[8]

3. Results and Discussion

As an illustration, we have chosen the trans $\rightleftharpoons$ cis rotational isomerization process, represented in Figure 2, of the following molecules obtained from simple substitution of the two H atoms by Cl atoms in the glyoxal molecule: (**1**) glyoxal, (**2**) Cl-glyoxal, and (**3**) oxalyl-Cl. The corresponding potential energy profiles along the torsional angle defined with respect to the central CC bond were obtained at the Hartree–Fock (HF) level with the standard 6-31G basis set and full optimization of the molecular geometry along the torsional angle. All calculations were performed using the Gaussian 94 package,[14] and the resulting torsional potential profiles along the torsional angle are displayed in Figure 3. It should be noted that the reduced reaction coordinate ω, which provides a general representation of any chemical reaction, can be defined by the torsional angle through a simple scaling procedure.[7] We note in Figure 3 that whereas glyoxal and Cl-glyoxal present double-well energy profiles with an energy barrier separating them, oxalyl chloride presents a topologically different profile. Here the cis conformation corresponds to an energy maximum.

Shown in Figure 1 is the bifurcation condition partitioning the parameter space in regions I and II, and in Figure 4 are given the different topologies displayed by the energy profile along the variable ω in each region, I and II, and on the bifurcation curve. As can be seen, in region I where molecules **1** and **2** lie, the quadratic term is predominant and only a nondegenerate critical point (maximum) is exhibited. These two molecules are therefore expected to behave according to the HP and PMH. On the bifurcation curve or separatrix, the critical point is 2-fold degenerate and a large *plateau* is displayed by the energy profile. By crossing that curve, in region II, the cubic term begins to be important, leading to the appearance of two nondegenerate critical points. This behavior is not isomorphous to any of the elementary catastrophes known (in particular, to the *fold* catastrophe). Reaction **3** lies in region II, and therefore it cannot be classified in terms of its HP and PMH behavior. In particular, the energy profile for the internal rotation of oxalyl chloride presents a minimum at the trans conformation and a maximum at the cis one. No TS between these two conformations is actually found. From the PMH requirements and eq 4, this behavior should also be expected in the hardness and chemical potential profiles.

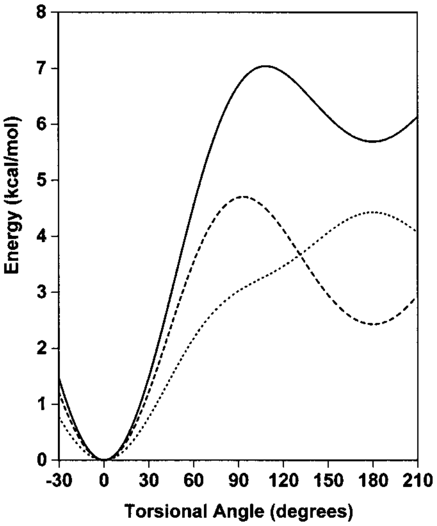

Figure 3. Ab initio HF/6-31G energy profiles along the torsional angle of glyoxal (—), Cl-glyoxal (– – –), and oxalyl chloride (···).

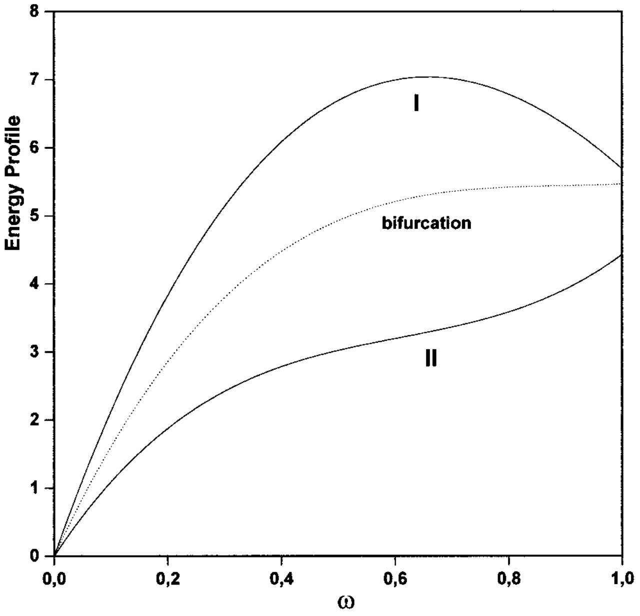

Figure 4. Different topologies displayed by the energy profile (in arbitrary units) in regions I and II, and on the bifurcation curve.

Some final conclusions drawn from this analysis concerning the behavior of the general profile expressed in eq 7 within the HP and PMH framework are very interesting. First, due to the relationships between local and global properties in the framework of DFT,[1] we expect the electronic density will also display bifurcation along the reaction coordinate ω. Additional local properties such as the Fukui function and, in general, any response function are also expected to present bifurcations. Important theoretical challenges in the rationalization of the reactivity indexes of chemical species are therefore open. Second, contrary to the usual view based upon the HP and PMH behavior, the present analysis shows that chemical processes can be globally classified in two main regions according to the topology exhibited by the reaction profile. Third, it is worth mentioning that the model developed here can be easily generalized to deal with intermolecular chemical reactions provided that the reaction coordinate could be described by a single reduced variable such as ω. Finally, fourth, due to the thermodynamic implications explicitly exposed in this work, the general function given by eq 7 could be considered as a first approximation to a more general and appealing function which we would like to propose, that is, a Gibbs-like potential:

$$G[\omega] = F[\omega] + \omega \ln \omega + (1 - \omega) \ln(1 - \omega) \qquad (12)$$

By applying an algorithm based on the catastrophe theory,[15] this function has been shown to display a canonical bifurcation which is isomorphous to the *fold* catastrophe. As is well-known, for the corresponding elementary catastrophe, the parameter space is one-dimensional and the separatrix between functions of two qualitatively different topologies is only a point. Thus, regions I and II are on both sides of that point, leading to a more simple scheme of classification of chemical reactions.

Acknowledgment. We thank the CSIC−CONICYT Exchange Project for visiting stays in Chile and Spain and acknowledge financial support from Cátedra Presidencial en Ciencias awarded to A.T.L., FONDECYT Project No. 1990543, and DGICYT Contracts PB96-0651-C03-01 and PB95-007.

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