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REVIEW ARTICLE

Understanding Reaction Mechanisms in Organic Chemistry from Catastrophe Theory Applied to the Electron Localization Function Topology

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Thom's catastrophe theory applied to the evolution of the topology of the electron localization function (ELF) gradient field constitutes a way to rationalize the reorganization of electron pairing and a powerful tool for the unambiguous determination of the molecular mechanisms of a given chemical reaction. The identification of the turning points connecting the ELF structural stability domains along the reaction pathway allows a rigorous characterization of the sequence of electron pair rearrangements taking place during a chemical transformation, such as multiple bond forming/breaking processes, ring closure processes, creation/annihilation of lone pairs, transformations of C−C multiple bonds into single ones. The reaction mechanism of some relevant organic reactions: Diels−Alder, 1,3-dipolar cycloaddition and Cope rearrangement are reviewed to illustrate the potential of the present approach.

Introduction

The concept of reaction mechanism plays a major role in chemistry representing a synthesis of our understanding on the way in which the bonding structure of a reactant is modified as the reaction proceeds. The description of the reaction mechanism associated with a given chemical reaction at the microscopic level is currently based on the calculation of the geometries and energies of the stationary along the reaction pathway points connecting reactants to products, via transition structures (TSs) and possible intermediates on the Born-Oppenheimer potential energy surface (PES).[1–5] However, theoretical chemistry should not be used only to obtain accurate data for the geometries, energies and spectroscopic properties of the proposed molecular structures. A very important part of quantum chemical research should be devoted to the rationalization of the results in terms of quantitative concepts derived from first principle calculations.

Since the introduction of the electron bond pair concept by Lewis more than 90 years ago[6,7] and the subsequent quantum mechanical treatment by London[8] and Pauling,[9] many methods and techniques have been developed for the understanding of structure and chemical reactivity. Along these years, quantum chemical tools based on both molecular orbital (MO) and valence bond (VB) theories have been proven to be extremely successful to chemists for the theoretical analysis of any kind of chemical reactions, yielding explicative models and ways of thinking which have been widely adopted within the chemical community. In the framework of both theories, different concepts have been used and developed to provide a general scheme to describe fundamental aspects of chemical structure and reactivity: in the MO approach the seminal applications of Dewar,[10] the Walsh diagrams,[11] the frontier orbitals of Fukui,[12] orbital symmetry rules of Woodward−Hoffman[13] and the concept of electron bond pair[14] and resonance structures that are characterized by localized chemical bonds are the basis of the VB theory developed by Slater and Pauling.[9,15–19] Nowadays, valence bond methods are employed for the calculation and analysis of reaction mechanisms,[20,21] determination of Lewis resonance structures,[21,22] description of electron-transfer processes,[23] or for dynamical explorations of the PES.[24] Also, modern versions of VB theory have been developed for the understanding of chemical reactivity such as the spin-coupled theory[25] or the breathing orbitals.[26] Recently, the past and the present of both MO and VB approaches have been expressed in a series of conversations to studying chemical bonds and reactivity in molecules.[27] Another important methodology developed for the understanding of electronic structure is based on the natural bond analysis of Weinhold et al.,[28–30] which has been also employed to analyze electronic rearrangements along chemical reactions. Other descriptions of chemical reactivity based on wave function procedures such as localized molecular orbitals[31] or the domain-averaged Fermi hole[32] have been also proposed. Insights into energetic aspects of activation barriers also can be gained by means of energetic decomposition analysis[33] employed for the evaluation of orbitalic and steric repulsion terms between defined fragments. The unified reaction valley approach developed Kraka et al.,[34] which combines the classical reaction path Hamiltonian[35] and the localized internal modes of Cremer et al.,[36] has been also employed for the investigation of reaction mechanisms. On the other hand, the

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development of reactivity indexes from concepts derived from density functional theory (DFT),[37] the so-called conceptual DFT[38] have opened new ways for predicting chemical reactivity on a theoretical basis.

Clearly, although much progress has been made in recent years and significant achievements have been accomplished, the characterization of chemical bond and the subsequent breaking/forming processes are not closed subjects.[39] As many other concepts used in chemistry, the chemical bond has a rather ambiguous definition because it does not rely on an observable in the sense of quantum mechanics but rather belongs to a representation of the matter at a microscopic level developed by the chemists at the beginning of the XXth century and earlier which therefore is not fully consistent with quantum mechanical principles. To reconcile the chemical description of matter with the postulates of quantum mechanics, it is necessary to build a mathematical model. However, this mathematical model is not unique because different spaces (geometrical direct space, momentum space, Hilbert space) as well as different mathematical theories external to quantum mechanics can be used for this purpose. The geometrical space description has been pioneered by Raymond Daudel with the loge theory[40–42] the application of which was limited by the requirement of evaluating the *N*-particle distribution function. The theory of dynamical systems[43] is a powerful method of analysis which has been convincingly introduced in chemistry by Richard Bader with the theory of atoms in molecules (AIM).[44] This theory performs a partition of the electron within the molecular space into basins associated to each atom and in which the information arise from the electron density distribution. The development of the AIM theory is at the origin important contributions to conceptual structural chemistry, such as the definition of the atom within a molecule, of the bond critical point, of the bond path and of the molecular graph.[45–48] This scalar field is particularly important because the electron density can be reconstructed from experimental data instead of being calculated from first principles.[49] Additionally, the AIM approach uses first and second derivatives of the electron density to divide a system in atomic regions and characterize the bond paths.[50,51] Although the chemical meaning of both paths have been recently been questioned,[52] a deeper understanding on the relationship between the bond path and chemical bonding has been provided by Pendas et al.[53] A further step in the analysis of chemical reactions using AIM theory was made by using the delocalization indexes of Fradera et al.[54] on some organic reactions.[55] AIM has been used in connection with Thom's catastrophe theory to study structural changes;[45,56] however, its application remains limited to isomerisation reactions because the dissociation of a diatomic molecule is not accompanied by any characteristic topological change. For this reason Malcolm and Popelier[57] have shown that the full topology of Laplacian of the electron density was associated with the electron pairs of the valence shell electron pair repulsion model of Gillespie.[58] In fact, the description provided by AIM is quite different from that of chemistry which considers a molecule as an assembly of atoms linked by bonds. An atom in a molecule consists of a core (the nucleus and the inner shell electrons) and of valence electrons gathered in the valence shell. The structure of the core and the possible numbers of electrons belonging to the valence shell are given by the position of the element in the periodic table. In general, a molecule has fewer electrons than the sum of the populations of the valence shells of its atoms because some of the valence electrons may be shared in two or more valence shells. Such electrons are said to be bonding electrons whereas the remaining valence electrons are non-bonding. The arrangement of the electrons in the valence shells constitutes the chemical electronic structure. In this description the bonding arises from shared electrons.

Another procedure provides a more straightforward connection than AIM between the electron density distribution and the chemical structure. It is the topological analysis of the Electron Localization Function (ELF) of Becke and Edgecombe.[59] This is also a scalar field that is different than the used by the AIM approach, because it is based in the second-order density matrix and is defined such that its values range between 0 and 1.[60] Recently, the ELF has been presented in a very chemical fashion and its topology can be used to revisit different phenomenological model of chemical bonding in molecules.[61] Another topological approach has been applied by Gadre et al.[62] on the scalar field derived from the molecular electrostatic potential for 1,3-dipolar cycloaddition reactions. Dynamical exploration of PES using topological criteria has also been carried out by Joubert and Adamo[63] on S_N2 reactions.

The characterization of electron pair rearrangements for describing the changes in the bonding scheme along the reaction pathway can be considered as the most desirable way to analyze a reaction mechanism. However, this description only can be obtained through a quantitative assessment of electronic pairing rather than intuitive or qualitative descriptions. Moreover, a robust mathematical treatment for the structural electronic changes is required when there is a change in the number or type of electron pairs. To fulfill these requirements, the bonding evolution theory (BET), consisting of the joint use of ELF and the catastrophe theory (CT) of Rene Thom[64–66] was proposed by Krokidis et al.[67] as a new tool for the contemporary understanding of electronic rearrangements in chemical processes and applied to different elementary reactions were studied such as proton transfers,[68] isomerisations,[69] electron transfers.[70] More recently the scope of applications of BET has been enlarged in two complementary directions. On the one hand, Russo in Italy initiated a series of studies on two-state reactivity[71–73] for which the approach has been very helpful for the characterization and the bonding description in the intermediates. Meanwhile, in Spain a systematic investigation was initiated of the mechanism of important organic reactions such as the Diels−-Alder reactions,[74,75] the 1,3-dipolar reaction between fulminic acid and acetylene,[76] the molecular mechanism of the Bergman cyclization,[77] the trimerization of acetylene,[78] the "chameleonic vs centauric" mechanisms of the Cope rearrangement of 1,5 hexadiene and its cyano derivatives,[79] the Nazarov cyclization,[80] and the S_N2 reaction.[81]

The examples shown in the present work are part of an ongoing effort to elucidate fundamental details of chemical reactivity and the present procedure opens an emerging scenario representing a definitive departure of the actual description of reaction mechanisms. Therein the focus is shifted on electron pair rearrangements such as bond formation/breaking processes, formation/annihilation of lone pairs or/and transformation among single/double/triple bonds taking place along the reaction pathway. The main goal of the present methodology is to find quantitative answers to the following questions: (i) How could the electronic reorganization proceed along the reaction path? (ii) Do the bond formation/breaking processes take place at the TS? (iii) When does the electron pair rearrangements take place along the reaction pathway? (iv) How can the electron flow be related to the electron-pair rearrangements? (v) Whose are the electron pairs involved in the electronic reorganization? (vi) Is it possible to distinguish between electron pairs playing active (actors) or passive (spectators) roles? (vii) How and in which extent do substituent effects modify the reaction mechanism? (viii) Do they produce a mere side effect or a definitively new electronic rearrangement?

The Mathematical Model

One of the aims of Lewis's theory of valence,[6,7] which is at the root of the chemical representation, is the prediction of the most probable structures with the help of additional rules such as the octet rule and the rule of two. Lewis's approach emphasizes the electron pair as a key concept. It is worth noting that any N electron system has at most $N/2$ pairs in the chemical description and $N(N - 1)/2$ in the quantum mechanical one. This apparent contradiction is a consequence of the indiscernability of identical particles and, rather than $N/2$ pairs one has to look for $N/2$ regions of space within which each integrated opposite spin electron pair density is close to 1 whereas the integrated same spin electron pair densities are small. There is no direct experimental proof of the existence of such regions. This model consists of a four electron system in a box of volume V. The system is in a singlet state and the electron density distribution is assumed to be constant and the integrated same spin pair densities in the right (A) and left (B) parts of the box are zero. The one electron and pair density distributions being α and β the one electron spin functions with the definitions of the textbook of McWeeny[82] have the following expressions:

$$\rho^{\alpha}(r) = \rho^{\alpha}(r) = \frac{2.0}{V} \qquad \text{for } r \in \text{A or B} \tag{1}$$

$$\begin{aligned}\pi^{\alpha\alpha}(\mathbf{r},\mathbf{r}') &= \pi^{\beta\beta}(\mathbf{r},\mathbf{r}') \\ &= \begin{cases} 0.0 & \text{for } \mathbf{r} \text{ or } \mathbf{r}' \text{ in the same box} \\ \dfrac{2.0}{V^2} & \text{for } \mathbf{r} \text{ and } \mathbf{r}' \text{ in different boxes} \end{cases}\end{aligned} \tag{2}$$

$$\pi^{\alpha\beta}(\mathbf{r},\mathbf{r}') = \pi^{\beta\alpha}(\mathbf{r},\mathbf{r}') = \frac{4.0}{V^2} \qquad \text{for } \mathbf{r} \text{ and } \mathbf{r}' \in \text{A or B} \tag{3}$$

Therefore the integrated opposite spin pair densities ($\alpha\beta$ and $\beta\alpha$) over a given volume v sample around any reference point are constant and equal to $4.0(v/V)^2$ whereas the integrated opposite spin pair densities are nonzero, if the sample belongs to both parts, in other words if it contains points of the boundary between parts A and B.

The spin pair composition[83] defined as

$$c_{\pi}(\mathbf{r}) = \overline{N}(\mathbf{r})^{-8/3}\overline{N}_{||}(\mathbf{r}) \tag{4}$$

where

$$\overline{N}(\mathbf{r}) = \int_{v(\mathbf{r})} \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{5}$$

and

$$\overline{N}_{||}(\mathbf{r}) = \int\int_{v(\mathbf{r})} (\Pi^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) + \Pi^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2))\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 \tag{6}$$

in which $\rho^{\alpha}(r)$ is the spinless one electron density distribution, $\prod^{\alpha\alpha}(r_1,r_2)$, $\prod^{\beta\beta}(r_1,r_2)$ is the ordered same spin pair functions (normalized to $N^{\alpha}(N^{\alpha} - 1)$ and $N^{\beta}(N^{\beta} - 1)$, respectively) and d$\mathbf{r}$ is the integration volume element. Hence, the spin pair composition provides is a trustable indicator of the presence of a boundary between localized pair regions. The $\overline{N}(r)^{-8/3}$ factor has been introduced to make $c_{\pi}(\mathbf{r})$ independent of the size of the sample. Unfortunately, the actual calculation of $c_{\pi}(\mathbf{r})$ is very lengthy and it was shown[83] that an excellent approximation is provided by the ELF function originally designed by Becke and Edgecombe.[59] Although originally the ELF was designed to measure the Fermi hole curvature calculated at the Hartree−Fock level, Savin's interpretation in terms of local excess kinetic energy due to Pauli repulsion[84] gave support to the calculation of ELF from Kohn−Sham orbitals. Other alternative interpretations of the ELF have been obtained in terms of localized orbitals[85] and recently as the nonadditive (inter orbital) Fisher information contained in the electron distribution.[86] Recently, a generalization of Dobson's interpretation has been achieved independently by Kohout et al.[40] and by Silvi[41] who introduced a more general localization functions, enabling the generalization of ELF to correlated wave functions.[87] In practice, the localization function adopts a Lorentzian form $\eta(\mathbf{r}) = (1 + c_{\pi}^{2}(\mathbf{r}))^{-1}$ which confines its values in the [1,0] interval.

The dynamical system theory is based on the analogy between a vector field of class C^1 bound on a manifold and a velocity field, i.e., in the present case:

$$\nabla\eta(\mathbf{r}) = \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} \tag{7}$$

Integrating d$\mathbf{r}$/dt with respect to the fictitious time variable t determines trajectories that start and end in the neighborhood of points at which the gradient vanishes, the α and ω limits, respectively. Of particular importance are the critical points P of coordinate $\mathbf{r}_P$ at which $\nabla\eta(\mathbf{r}_P) = 0$ and which are characterized by their index I_P, i.e., the number of positive eigenvalues of the second derivative (Hessian) matrix. A critical point is said hyperbolic when all the eigenvalues of the Hessian matrix

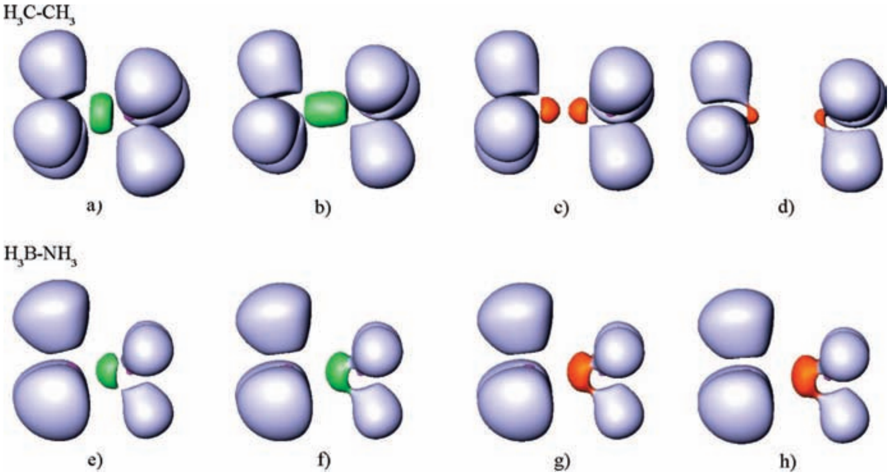


Figure 1. ELF topology for four molecular structures along the dissociation process of the C−C and B−N bonds in C_2H_6 (a)−(d) and BH_3NH_3 (e)−(h), respectively. Color legend: core, purple; monosynaptic, orange; disynaptic, green; hydrogenated, blue.

differ from zero. The set of points by which are built trajectories having a given critical point P as ω limit is called the stable manifold of P. It is therefore possible to achieve the partition of the geometrical space occupied by a molecule into basins of attractors, in other words into stable manifolds of critical points of index 0.

The topological partition of the ELF gradient field yields basins of attractors that can be identified as corresponding to atomic cores, bonds and lone pairs. In a molecule one can find two types of basins: (i) core basins surrounding nuclei with atomic number $Z > 2$ and labeled C(A) where A is the atomic symbol of the element; (ii) valence basins that are characterized by the number of atomic valence shells to which they participate, or in other words by the number of core basins with which they share a boundary. This number is called the synaptic order. Thus, there are monosynaptic, disynaptic, trisynaptic basins and so on. Monosynaptic basins, labeled V(A), correspond to the lone pairs of the Lewis type or nonbonding regions. A basin is disynaptic if it connects the core of two nuclei A and X and, thus, corresponds to a bonding region between A and X and labeled V(A,X). The valence shell of a molecule is the union of its valence basins. The valence shell of an atom, e.g., A, in a molecule is the union of the valence basins whose label lists contain the element symbol A. This description recovers Lewis's picture of the bonding[6,7] and provide very suggestive graphical representations of molecular systems. A quantitative analysis is further achieved by integrating the electron density and the pair functions over the volume of the basins yielding both basin populations and the corresponding covariance matrix,[89] which measures the electron and support a phenomenological interpretation in terms of weighted mesomeric structures.

The ELF depends on a set of parameters such as the nuclear coordinates, the electronic state, the interaction with an external field,[90] referred as the control space. The topology depends therefore obviously of the value of the control space parameters. The changes are ruled by the Poincaré−Hopf theorem, which states that

$$\sum_P (-1)^{I_P} = 1 \tag{8}$$

introducing a very strong constraint due to the structure of the geometrical space. The reaction pathway is traced following the intrinsic reaction coordinate (IRC) of Fukui,[91] which connects the stationary points on the PES, from reactives to products crossing the transition structure. Then, the reaction mechanism is determined by the topological changes of the ELF gradient field along a series of structural stability domains (SSDs). Within each SSD all the critical points are hyperbolic and separated by catastrophe or turning points (TPs) where at least one critical point is nonhyperbolic. The bifurcation catastrophes occurring at these TPs are identified according to Thom's classification,[64] which gives access to their unfolding, a compact polynomial expression that contains all the information about how ELF may change as the control parameters change. In this way, a chemical reaction is viewed as a sequence of SSDs connecting by TPs which can be identified to chemical events such as bond forming/breaking processes, creation/annihilation of lone pairs and other types of electron pair rearrangements.

Only three elementary catastrophes have been recognized so far in the studied chemical reactions: the fold, cusp and elliptic umbilic catastrophe. The fold catastrophe (see Figure 1a) transforms a wandering point (i.e., a point which is not a critical one) into two critical points of different parity. Its unfolding is $x^3 + ux$, x is the direction of the eigenvector corresponding to the eigenvalue of the Hessian matrix which changes of sign and u is the control space parameters which governs the discontinuity. The cusp catastrophe (see Figure 1b) transforms a critical point of a given parity into two critical points of the same parity and one of the opposite parity. Finally, the elliptic umbilic catastrophe changes the index of one critical point by 2.

The sequence of TPs occurring along the reaction pathway is represented by the general formula $N_1 - N_2 - \textbf{FCSHEBP} - N_3$ introduced by Berski et al.[75] In this notation N_1 is the ordinal number of an analyzed sequence that can be omitted when only one reaction is considered (i.e., $N_1 = 1$), N_2 is the number of observed steps associated to the SSDs usually greater than the number of catastrophes, FCSHEBP are the symbols of the catastrophes taken from their first letter in the original Thom's classification, i.e., $\mathbf{F}$ = fold, $\mathbf{C}$ = cusp, $\mathbf{S}$ = swallow tail, $\mathbf{H}$ = hyperbolic umbilic, $\mathbf{E}$ = elliptic umbilic, $\mathbf{B}$ = butterfly and $\mathbf{P}$ = parabolic umbilic, and N_3 indicates the end of the sequence. TPs of the same type occurring simultaneously are indicated by $[A]_n$, where n is the multiplicity of the catastrophe labeled by A. Moreover, bold symbols are used to emphasize the first bond formation whereas the † superscript is used for those catastrophes that increase either the number of basins or the synaptic order. For example, $C^\dagger$ corresponds to a cusp catastrophe in which an attractor gives rise to two new attractors and a saddle point of index 1. In this way, a chemical reaction can be decomposed in a well-defined sequence of electron pair topologies which can be identified with chemical concepts commonly used.

Application of the Bonding Evolution Theory to Chemical Reactions

Organic chemical reactions usually involve multiple electron-pair rearrangements associated to bond breaking/formation processes, creation/annihilation of lone pairs, and reduction of double bonds into single ones, among others. With the main goal of a quantitative analysis of these chemical events along a chemical reaction, the BET was proposed yielding a clear and comprehensive understanding on the electronic rearrangements and giving support to qualitative descriptions of reaction mechanisms using classical curly arrows. To illustrate the capabilities of the BET, three key organic reactions will be reviewed in this section, yielding a consistent and universal picture of the progressive transference of electronic charge between basins which precedes the arising of a turning point and the relationship with electron pair rearrangements.

Diels−Alder Reaction

The Diels−Alder reaction can be considered as one of the most important types of organic reactions. However, the molecular mechanisms of these type of reactions is not free of the most heated and interesting controversies. The BET analysis of the prototype Diels−Alder reaction (ethylene and butadiene) has been investigated by Berski et al.[74] Figure 2a displays the reaction path traced by the IRC and the location of each turning point, which delimits each SSD, and the populations of ELF valence basin along the same IRC path are reported in Figure 2b. On the basis of the variations of the ELF topology along the reaction path, seven SSDs (I−VII) are found which correspond to the $7\text{-}[\mathbf{C}]_2\mathbf{C}[\mathbf{F}^\dagger]_2[\mathbf{F}^\dagger]_2[\mathbf{C}]_2\mathbf{C}^\dagger\text{-}0$ sequence of TPs.

Figure 3a shows the ELF basins at different SSDs along the reaction path. At the first step of the reaction there is a mutual polarization of both molecules due to the Pauli repulsion producing a bond equalization process at the butadiene moiety by a transfer of electronic charge from double bonds to the single one. This process is characterized by cusp type TPs where the two disynaptic basins, $V_{1,2}(C_1,C_2)$ and $V_{1,2}(C_3,C_4)$, collapse into monosynaptic ones, $V(C_1,C_2)$ and $V(C_3,C_4)$. On the ethylene moiety it can observed a severe polarization of the disynaptic basins as a result of the closed-shell repulsion with the approaching butadiene molecule. After these processes, monosynaptic basins $V(C_5)$ and $V(C_6)$ are formed at terminal atoms (see Figure 3) followed by formation of C_1-C_5 and C_4-C_6 bonds and the subsequent ring closure process via cusp type TPs. It is worth noting that the pyramidalization of the terminal CH_2 groups is more pronounced for the ethylene fragment than for the butadiene moiety as it can be observed by the earlier appearance of the $V(C_5)$ and $V(C_6)$ than the $V(C_1)$ and $V(C_4)$ basins. According to the local electronic structures, terminal CH_2 tend to adopt the Gillespie′s AX_3E notation, which provides a phenomenological explanation for the formation of the monosynaptic basins on terminal carbon atoms.

The TS found on the PES does not correspond to any TP, but a relatively large value of $\eta(\mathbf{r}) = 0.49$ is found for the critical point of index 1 in the $C_1\cdots C_6$ and $C_4\cdots C_5$ regions, indicating a favorable electronic delocalization between both moieties. From the topological view on the ELF, the formation of new C_1-C_6 and C_4-C_5 bonds between 1,3-butadiene and ethylene occur at an interatomic distance of 2.044 Å by means of two cusp-type TPs. This type of analysis clearly shows the validity of the Hammond postulate because the topology of the TS is closer to reactants than to the products, in agreement with the exothermicity of the reaction. The reported data based on the BET analysis supports the reaction mechanism depicted in Scheme 1, where the curly arrows represent the reorganization of the electron pairs.

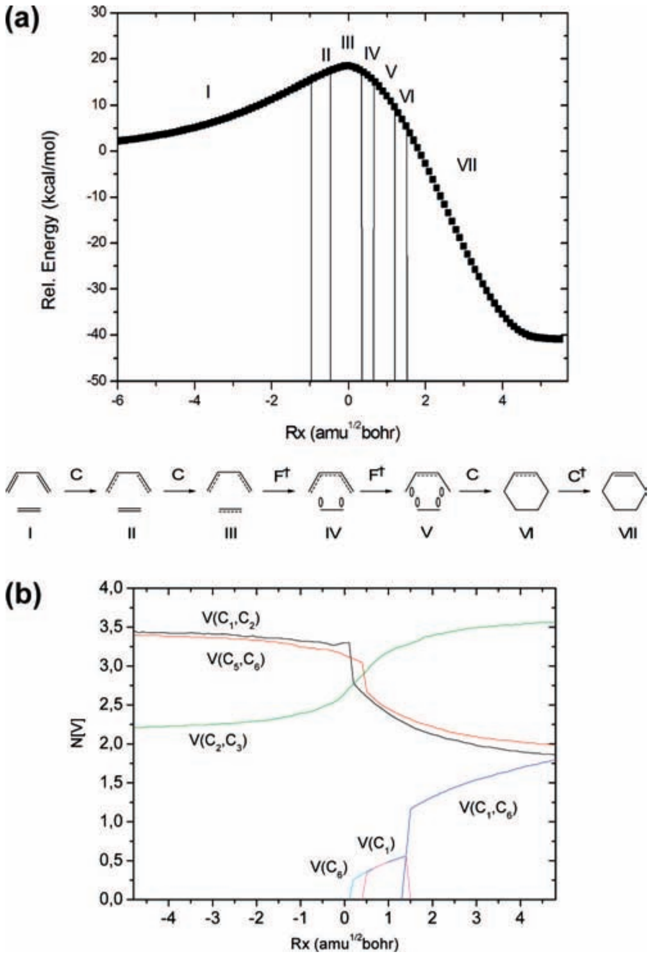
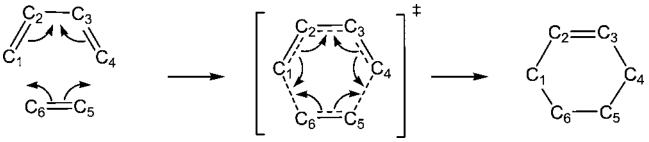


Figure 2. (a) IRC path for Diels−Alder reaction between 1,3-butadiene and ethylene indicating the structural stability domains (top), ELF topology of each domain (I−VII) is depicted together to the turning points (bottom). (b) Integration of ELF valence basins along the IRC path for Diels−Alder reaction between 1,3-butadiene and ethylene.

SCHEME 1



Recently, the substituent effects and presence of Lewis acid in two Diels−Alder type reactions, i.e., normal electron demand between 1,3-butadiene and acrolein and inverse electron demand between 2,4-pentadienal and methyl vinyl ether, have been investigated.[75] The electron redistribution during reaction course can be viewed as two mutual effects: the “ring effect” associated with the electron flux within the six-membered ring which is large and regular, and small and irregular the “side chain effect” appearing in the substituents. It is worth noting that these studies revealed that the presence

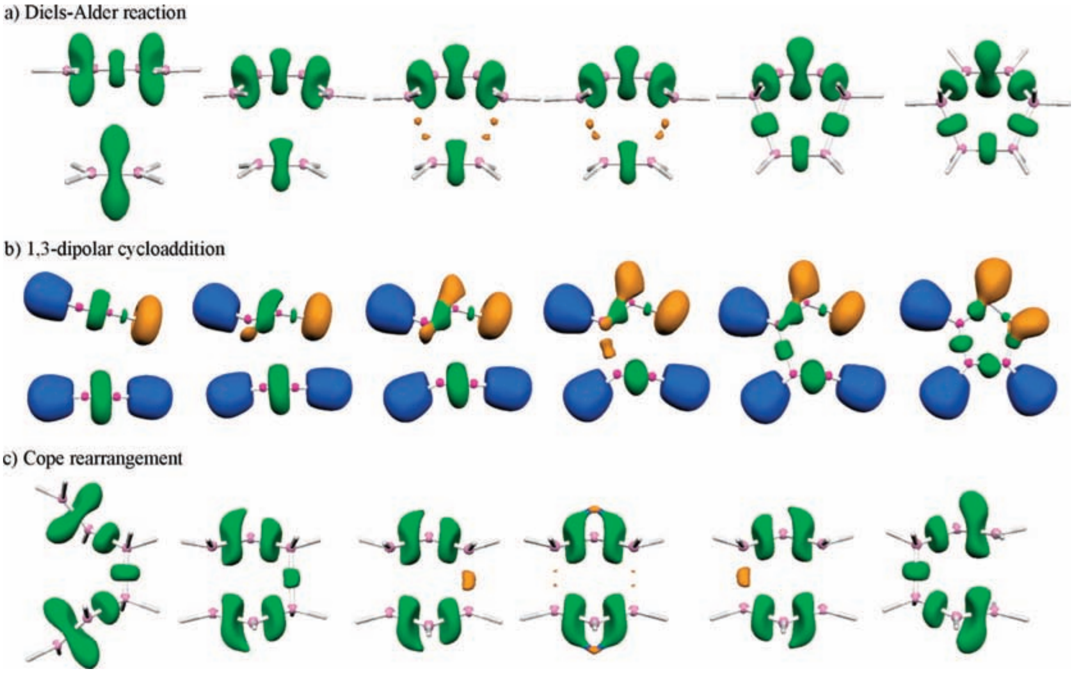


Figure 3. Snapshots of the ELF basins for the Diels−Alder reaction of 1,3-butadiene with ethylene (a), 1,3-dipolar cycloaddition of fulminic acid and acetylene (b), and Cope rearrangement of hexa-1,5-diene (c). Color legend: core, purple; monosynaptic, orange; disynaptic, green; hydrogenated, blue. Hydrogenated basins are not shown in (a) and (c) for clarity.

of electron-withdrawing susbtituents on either 1,3-butadiene or ethylene breaks the concerted character of the butadiene-ethylene Diels-Alder reaction.

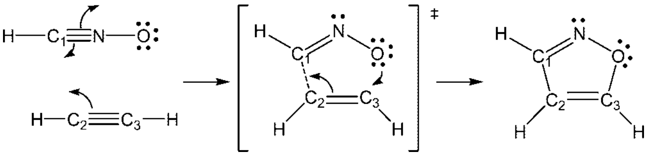
1,3-Dipolar Cycloaddition

The nature of the molecular mechanism of the 1,3-dipolar cycloaddition between fulminic acid and acetylene has been object of controversies since its discovering by Huisgen[92] due to the concerted/stepwise dichotomy,[93] to the discussions on the sense of electronic charge flowing.[94–97] The involvement of polarized bonds between atoms of different electronegativity and lone pairs complicates the analysis of the reaction mechanism.

This chemical rearrangement can be viewed as a transfer of electron density from the reactant-like basins into three newly created basins, which represent two chemical bonds between the reactants and a lone pair on N in seven steps characterized by catastrophe theory (see Figure 4a for the energy profile along the IRC path). The sequence of TPs of the 1,3-dipolar cycloaddition of fulminic acid and acetylene corresponds to $7\text{-}\mathbf{F}^{\dagger}\mathbf{F}^{\dagger}\mathbf{CF}^{\dagger}\mathbf{F}^{\dagger}\mathbf{C}\text{−}0$. Following the increments/decrements of electronic populations of ELF basins along the reaction path represented in Figure 4b, the order in which new chemical entities are created as well as their precedence can be determined.

The first step of the reaction is clearly driven by the low frequency modes of the reactants that are responsible for the fold catastrophes giving rise to the monosynaptic basins $V(C_1)$, $V(N)$ and $V(C_2)$, and leading to the activated complex. Interestingly, the ELF analysis shows that the lone pair at nitrogen atom arises from the C_1-N bonding basin, not from the $N-O$ bond (see Figure 3). The activated complex formation is then achieved through a cusp catastrophe which merges $V(C_1)$ and $V(C_2)$ into $V(C_1,C_2)$ or, in other words, forming a covalent C_1-C_2 bond. The ring closure is described as dative process in which the oxygen atom shares an electron pair yielding a strongly polarized C_3-O bond (see Figure 3). The present analysis shows than the lone pairs of O remain inactive until the last part of the reaction path. The described sequence of ELF topologies supports the description of the reaction mechanisms provided in the Scheme 2.

SCHEME 2



Characterization of Borderline Mechanisms: The Cope Rearrangement

There are many cases in chemical reactivity where the reaction mechanism is a borderline between two competing reactive channels. Small perturbations that apparently may be external to the atoms involved in the reaction process, like hydrogen bond formation or substituent effects, can modify the flow of electron density along the reaction path changing from mechanism into another. A paradigmatic case of this kind of reactions is the Cope rearrangement and the so-called “chameleonic” mechanism.

The Cope reaction of 1,5-hexadiene is a thermally allowed [3,3] sigmatropic shift involving the migration of a σ bond along one or two π systems. Recently, Polo and Andres[79] have carried out a comprehensive work to gain new insights about the role of the cyano substituents and their influence on the reaction mechanism of the Cope rearrangement of 1,5-hexadiene and its cyano derivatives. The BET analysis of the unsubstitued reaction reveals that the main TPs take place in the immediately vicinities of the TS; see Figure 5a. The analysis of the ELF at the TS shows the presence of six monosynaptic basins (one per carbon atom) enclosed by an isocontour surface of high ELF value (0.74) (see Figure 3). The BET analysis of the reaction

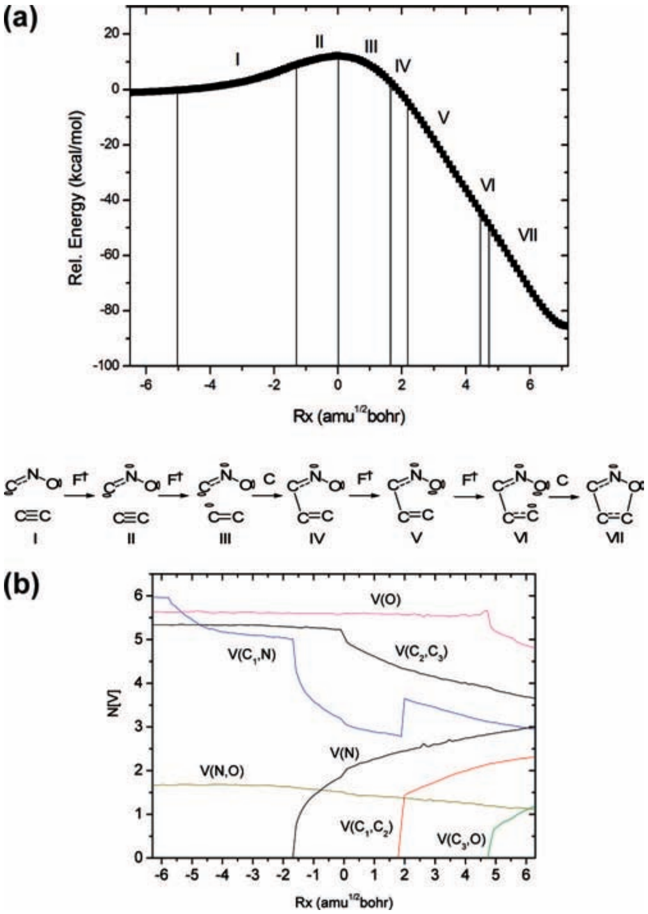
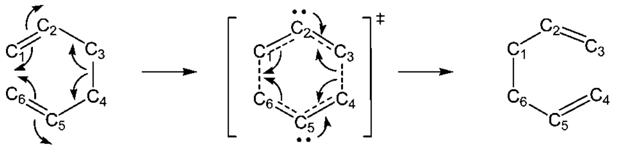


Figure 4. (a) IRC path for 1,3-dipolar cycloaddition of fulminic acid and acetylene indicating the structural stability domains (top), ELF topology of each domain (I−VI) is depicted together to the turning points (bottom). (b) Integration of ELF valence basins along the IRC path for the 1,3-dipolar cycloaddition of fulminic acid and acetylene.

SCHEME 3



path supports the electronic motions depicted in Scheme 3. Monosynaptic basins can be considered as precursors of bond formation or lone pair creation and different rearrangements of the V(C) can be possible. This particular ELF topology indicates that the nature of the TS can be altered very easily at it is done using cyano substituents at key positions.

The presence of a cyano on $C_{2,5}$ atoms stabilizes resonance structures with non-bonding electrons on terminal carbons ($C_{1,3,4,6}$), favoring the formation of $C_1{-}C_6$ bond and penalizing the breaking of $C_3{-}C_4$ bond process. Hence, a stepwise reaction mechanism via a stable cyclohexane biradical intermediate can be followed if cyano groups are placed on C_2 and C_5 atoms. On the other hand, if the substitution pattern takes place on $C_{1,3,4,6}$ atoms, there is an acceleration of the electronic charge coming from the breaking process of $C_3{-}C_4$ bond by delocalization onto the cyano groups. The description obtained by the ELF analysis provides support for the electronic movements represented in the Scheme 3. Hence, a change on the reaction mechanism from a diradicalod TS to a bis-allyl intermediate can be achieved. The sequence of TPs of the unsubstitued Cope rearrangement corresponds to $9\text{-}[\mathbf{C}]_2\mathbf{C}^{\dagger}[\mathbf{F}^{\dagger}]_2[\mathbf{F}^{\dagger}]_2[\mathbf{F}]_2[\mathbf{F}]_2\mathbf{C}\text{-}[\mathbf{C}^{\dagger}]_2{-}0$. Interestingly, our analysis shows how cyano substituents regulate the flow of electronic density charge along the reaction path leading to complete different electronic reaction mechanism. The ELF and CT description of substituted reactions reveals the different ordering of the sequence of TPs, changing the mechanism from a diradicaloid TS to a bis-allyl intermediate or even a compromise structure between these two, the so-called “centauric” mechanism.

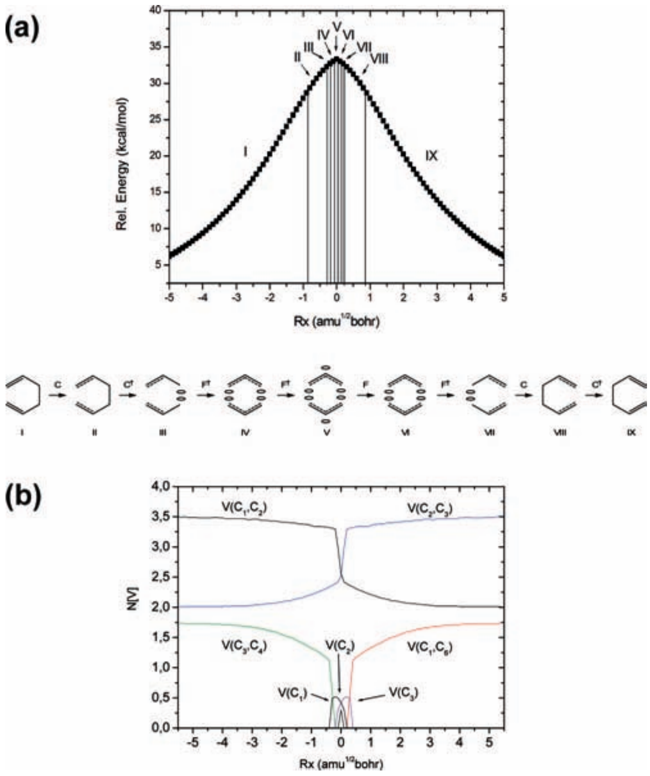


Figure 5. (a) IRC path for Cope rearrangement of hexa-1,5-diene indicating structural stability domains (top), ELF topology of each domain (I-IX) is depicted together to the turning points (bottom). (b) Integration of ELF valence basins along the IRC path for the 1 Cope rearrangement of hexa-1,5-diene.

Conclusions

The present work takes advantage of the joint use of both the Thom′s catastrophe theory (CT) and electron localization function (ELF) of Becke and Edgecombe as a new tool for tackling the study of electronic rearrangements in reaction mechanisms. On the basis of both a quantum mechanical observable (electron density) and a mathematical basis for CT and the universal behavior that it predicts, this methodology can be employed for a wide range of possible applications. Hence, an appropriate procedure for the understanding and classification of changes in the electronic structure and its implications into the energy and the geometry of the species involved in a given chemical reaction is obtained. The ELF provides a partition of the space into basins which can be associated to classical chemical objects such as electron cores, chemical bonds, and lone pairs. This representation allows us to recover the picture of Lewis mesomeric structures whose weighted combination is determined by the mean populations of the ELF basins. Following this way, changes on the ELF topology can be studied along the reaction path, traced by the intrinsic reaction coordinate (IRC), allowing define a structural stability domains (SSDs) as a region of the potential energy surface presenting the same ELF topological features. Those points connecting two SSDs are the so-called turning points (TP) which can be characterized from CT and can be associated to chemical concepts. Hence, cusp or fold type TP corresponds to a covalent or dative bond breaking/formation if they transform a disynaptic basin into monosynaptic one(s). Other chemical events such as creation/annihilation of lone pairs, transformation among single/double/triple bonds can also be characterized by TPs. Within this framework, the electronic rearrangements along a chemical reaction can be determined by the sequence of SSDs crossed by the reaction path.

In summary, the present approach is an appropriate tool in the contemporary understanding of the electronic principles governing chemical reactivity and some important questions are elucidated: (i) Quantitative analysis of the evolution of electron pairs along the reaction pathway. The movement of the electron pairs can be determined by following the flows of electron density charge between the ELF basins. (ii) The SSDs along the reaction pathway are ruled out by TPs which determine the appearance/annihilation of basins. (iii) From this analysis, concepts such as bond breaking/forming processes, formation/annihilation of lone pairs and other electron-pair rearrangements arise naturally along the reaction progress simply in terms of the different ways of pairing-up the electrons. (iv) A clear correspondence between the structures, derived from valence shell electron pair repulsion model of Gillespie, and topology can be directly achieved. (v) It is now possible to obtain highly accurate results while retaining a clear-cut visualization of each particular chemical event along the reaction pathway, demonstrating how new light can be shed on longstanding issues in chemical reactivity. (vi) It is thus clear that the present theory of chemical reactivity basically relies on the knowledge of topology and properties of SSDs presented along the reaction pathway on the potential energy surface. Various representative applications have been described in this work, indicating both the generality and utility of the analysis.

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