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The reaction electronic flux in chemical reactions

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The mechanism of a chemical reaction can be characterized in terms of chemical events that take place during the reaction. These events are bond weakening/breaking and/or bond strengthening/forming. The reaction electronic flux (REF), a concept that identifies and rationalizes the electronic activity taking place along the reaction coordinate, has emerged recently as a powerful tool for characterizing the mechanism of chemical reactions. A quantitative theory introducing new descriptors for characterizing reaction mechanisms is presented in detail and three illustrative examples are revisited. In nucleophilic substitution reactions the REF indicates that bond breaking or forming events may be leading the electronic activity whereas in the methanol decomposition reaction by copper oxide, the REF allows to discover that consecutive electronic reductions of copper together with bond breaking processes control the course of the reaction.

reaction mechanisms, chemical potential, conceptual DFT, reaction electronic flux (REF)

1 Introduction

The course of a chemical reaction involving one or more individual steps is a very complex process. It is commonly described by the minimum energy path that links the transition state to the reactants and products and defines the intrinsic reaction coordinate ξ. The intrinsic reaction coordinate is obtained by applying the classical equations of motion that leads to the energy profile $E(\xi)$ [1–3]. Recently, the reaction force concept has been introduced as a framework to analyze the mechanism of chemical reactions. It is the negative of the derivative of the potential energy $E(\xi)$ with respect to the reaction coordinate [4–7]:

$$F(\xi) = -\frac{\mathrm{d}E}{\mathrm{d}\xi} \qquad (1)$$

For a generic potential function presenting an energy barrier separating the reactants, located at ξ_R, and the product at ξ_P, $F(\xi)$ exhibits two critical points (at points ξ_1 and ξ_2).

These are used to define three reaction regions along ξ: the reactant region ($\xi_R \leqslant \xi \leqslant \xi_1$) where the reactants are prepared for the reaction mainly through structural reordering; the transition state region ($\xi_1 < \xi < \xi_2$) which is characterized by a marked electronic reordering, and the product region ($\xi_2 \leqslant \xi \leqslant \xi_P$) that is mainly characterized by structural relaxation leading to the products [6–10]. The reaction regions are guidelines to localize specific effects that might be operating during the reaction. The characterization of the nature of these effects, mainly structural and/or mainly electronic, allows to understand a chemical reaction in terms of changes in structural and electronic properties that occur in going from the reactants to the products.

It is worth mentioning that the reaction force analysis indicates that it is more realistic to think of a process as going through a transition state region rather than focusing upon a single point transition state [11]. This idea is consistent with modern definitions of a transition state from transition state spectroscopy (TSS) [12, 13]. In TSS the transition state is a region encompassing all of the states of the system, from perturbed forms of the reactants to perturbed forms of the

products.

In this paper the above defined reaction regions are used as a framework to analyze the electronic activity that takes place during a chemical reaction. This activity will be characterized through the reaction electronic flux [14–18].

2   The reaction electronic flux (REF)

The electronic chemical potential (μ) is a key property to understand the changes of the electronic structure during a chemical reaction. It accounts for the escaping tendency of electrons from an equilibrium distribution. Chemical potential arises in the Euler-Lagrange equation of the energy functional of Density Functional Theory (DFT) as a Lagrange multiplier to comply with the condition that the electronic density integrates to N, the total number of electrons of the system [19,20]. One important characteristics of μ is actually its link with the electronegativity χ [20–24] ($\chi = -\mu$) and the Sanderson's electronegativity equalization principle [25, 26] that has been used to characterize formation reactions that reach the equilibrium state after equalization of the chemical potentials of the different fragments that form the final molecule [27].

It is conceptually useful to examine the profile of the chemical potential that for a N electron system with total energy E and external potential $v(\vec{r})$ is defined as [23]:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} = -\chi \tag{2}$$

Owing to the discontinuity of the variable N, chemical potential can be computed through the use of finite difference approximation and the Koopman's theorem through the following expressions [28, 29]:

$$\mu \approx -\frac{1}{2}(IP + EA) \approx \frac{1}{2}(\epsilon_H + \epsilon_L) \tag{3}$$

where IP is the first ionization potential, EA is the electron affinity; ϵ_H and ϵ_L are the energies of the highest occupied and lowest unoccupied molecular orbitals, HOMO and LUMO, respectively. By evaluating μ along the reaction coordinate it is possible to determine the profile $\mu(\xi)$ that shows the evolution of the chemical potential during the chemical reaction. The reaction electronic flux (REF) associated to a chemical reaction is defined as [14–18]:

$$J(\xi) = -\frac{\mathrm{d}\mu}{\mathrm{d}\xi} \tag{4}$$

thus placing the REF as a measure of the electronic activity taking place along the reaction coordinate. In analogy with classic thermodynamics, $J(\xi)$ can be used to describe the spontaneity of the electronic activity during the reaction [17]. Positive values of $J(\xi)$ accounts for spontaneous changes in the electronic density which are related with bond strengthening or forming processes whereas negatives values

of $J(\xi)$ are indicating non-spontaneous electronic reordering that should be associated with bond weakening or breaking processes [17].

The reaction electronic flux also gives phenomenological insights on the electronic activity taking place during a chemical reaction by rationalizing the electronic activity in terms of polarization and electronic transfer contributions J_p and J_t [14–18, 30]:

$$J(\xi) = J_p(\xi) + J_t(\xi) \tag{5}$$

Numerically J_p can be determined by making a rational partition of the reactive complex in molecular fragments such that the polarization flux is defined as the sum of the fragments fluxes. For a n-fragment system it is given by [18]

$$J_p(\xi) = \sum_{i=1}^{n} J_p^{(i)}(\xi) \tag{6}$$

Each $J_p^{(i)}(\xi)$ is obtained separately using the counterpoise method [31, 32]. In this procedure, at each point point along ξ, counterpoise calculations are performed to obtain the fragment's chemical potential $\mu_i(\xi)$, thus leading to:

$$J_p^{(i)}(\xi) = -\left(\frac{N_i}{N}\right)\frac{\mathrm{d}\mu_i}{\mathrm{d}\xi} \tag{7}$$

where N_i is the number of electrons of fragment i and N is the total number of electrons of the supermolecular system. In this way the contribution to J_p coming from each fragment remains proportional to its own number of electrons.

The flux associated to electronic transfer is obtained by making the difference between $J(\xi)$ calculated using the supermolecule approximation and $J_p(\xi)$ calculated from the isolated fragments using the counterpoise method:

$$J_t(\xi) = J(\xi) - J_p(\xi) = -\frac{\mathrm{d}\mu}{\mathrm{d}\xi} + \sum_{i=1}^{n}\left(\frac{N_i}{N}\right)\frac{\mathrm{d}\mu_i}{\mathrm{d}\xi} \tag{8}$$

To obtain the fragment contribution to J_t and J, the principle of equalization of the chemical potential has to be invoked [25, 26]. Since the chemical potential is a global property of the system, within the supermolecule $\mu_i = \mu$, for all fragments. The chemical potential of the supermolecule can be expressed in terms of fragment's chemical potentials as:

$$\mu(\xi) = \sum_{i=1}^{n}\left(\frac{N_i}{N}\right)\mu_i(\xi) \tag{9}$$

and eq. (4) can be written as:

$$\begin{aligned} J(\xi) = -\frac{\mathrm{d}\mu}{\mathrm{d}\xi} &= -\sum_{i=1}^{n}\left(\frac{N_i}{N}\right)\frac{\mathrm{d}\mu_i}{\mathrm{d}\xi} \\ &= -\sum_{i=1}^{n}\left(\frac{N_i}{N}\right)\frac{\mathrm{d}\mu}{\mathrm{d}\xi} = \sum_{i=1}^{n} J^{(i)}(\xi) \end{aligned} \tag{10}$$

Finally the flux associated to electron transfer among the fragments is given by:

$$J_t(\xi) = J(\xi) - J_p(\xi)$$

$$= \sum_{i=1}^{n} \left(\frac{N_i}{N}\right)\frac{\mathrm{d}\mu_i}{\mathrm{d}\xi} - \sum_{i=1}^{n} \left(\frac{N_i}{N}\right)\frac{\mathrm{d}\mu}{\mathrm{d}\xi}$$

$$= \sum_{i=1}^{n} \left(\frac{N_i}{N}\right)\frac{\mathrm{d}}{\mathrm{d}\xi}(\mu_i - \mu)$$

$$= \sum_{i=1}^{n} J_{\mathrm{t}}^{(i)}(\xi) \tag{11}$$

It features a difference of chemical potentials, a clear signature of electronic transfer. It is important to note that $\mu_i(\xi)$ comes out from the calculation of the isolated fragment i, keeping the geometry it has in the supermolecule at point ξ and $\mu(\xi)$ results from the supermolecule calculation. It is also important to stress the fact that the reaction electronic flux emerges as a very flexible tool to characterize the mechanism of chemical reactions: it can be analyzed from the phenomenological viewpoint through the partition into polarization and transfer effects, displayed in eq. (5); on the other hand, it gives crucial chemical information about the electronic activity taking place within the reactive fragments involved in the chemical reaction, as shown in eqs. (7), (11) and (12):

$$J(\xi) = J_{\mathrm{p}}(\xi) + J_{\mathrm{t}}(\xi)$$
$$= \sum_{i=1}^{n} \left[J_p^{(i)}(\xi) + J_{\mathrm{t}}^{(i)}(\xi) \right] = \sum_{i=1}^{n} J^{(i)}(\xi) \tag{12}$$

thus indicating that $J^{(i)}(\xi) = J_{\mathrm{p}}^{(i)}(\xi) + J_{\mathrm{t}}^{(i)}(\xi)$, for all fragments of the system. In this context the reaction electronic flux accepts the double and simultaneous scrutiny of the chemical fragments and the physical phenomenon.

3　Results and discussion

In this section we will discuss three representative examples of the use of the reaction electronic flux to understand the mechanism of chemical reactions.

3.1　Nucleophilic substitution reactions

As a first illustration of the use of the reaction electronic flux, let us consider the key step involving the ion-dipole complexes of the symmetric nucleophilic substitution reaction $CH_3Cl + HCl \rightarrow CH_3Cl + HCl$. The energy barrier for this step is 8.43 kcal/mol [15]. The REF for this reaction is displayed in Figure 1(a) where it can be observed that the reaction starts with a zero regime REF. The electronic activity shows up within the reactant region and displays a maximum when entering the transition state region, a positive peak indicating that spontaneous Cl—C bond formation drives the electronic activity until reaching the transition state structure. Then the reaction electronic flux is driven by the non-spontaneous breaking process.

As a second example of the REF analysis, consider the nucleophilic substitution reaction $CH_3Cl + H_2O \rightarrow CH_3OH +$
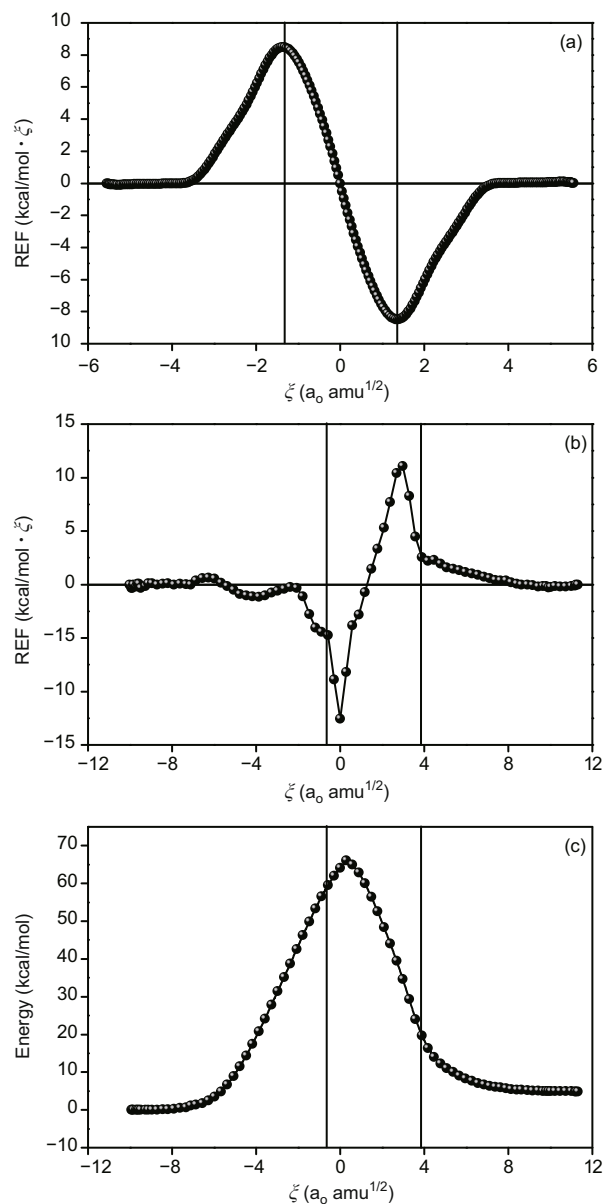
Figure 1　Reaction electronic flux profiles for reaction (a) $CH_3Cl + HCl$ and (b) $CH_3Cl + H_2O$; Figure 1(c) displays the energy profile of the latter reaction. Vertical bars indicate the limits of the reaction regions defined by positions ξ_1 and ξ_2, see the text for more details.

HCl. At the CCSD(T) level this reaction presents an energy barrier of 67 kcal/mol in the gas phase. The values of chemical potential were approximated using the HOMO and LUMO energies, as indicated by eq.(3) [33]. Figure 1(b) shows the REF profile along the intrinsic reaction coordinate [9, 33, 34] and Figure 1(c) displays the energy profile for this reaction.

It can be observed in Figure 1(b) that the reaction initiates with practically no electronic activity. This starts to emerge only at $\xi \approx -2.0$, when the reaction is quite advanced. A simultaneous analysis of the REF and energy profiles reveals that at least two third of the energy barrier should be safely associated to structural arrangements. Figure 1(b) shows the greatest variation of the REF within the transition state region

and identifies this as the region presenting the highest electronic activity, this activity should be responsible for about one third of the activation energy. In this way, the REF analysis helps elucidate the physical nature of the activation energy.

Phenomenologically, a negative peak in the REF profile, as the one observed within the transition state region, indicates that non-spontaneous bond breaking processes lead the electronic reordering. As the reaction continues, just after the transition state structure, a positive peak indicates spontaneous electronic activity due to the bond formation process. Finally, at the product region the electronic activity ceases and the structural relaxation takes over to reach the products of the reaction.

In summary, both S_N2 reactions studied in this paper start with the initial approximation of the molecules in a structural cortege with almost no electronic activity; in both cases the electronic activity starts up when leaving the reactant region and it is more intensive within the transition state region. Bond breaking or forming events drive the electronic reordering that slows down at the product region where the structural relaxation leads to the product conformations.

3.2 Methanol decomposition reaction

In this section a more complex reaction will be treated in the light of the reaction electronic flux. We will discuss the methanol decomposition by copper oxide [35, 36] using a model representing the initial step of the reaction $CH_3OH + CuO$ to produce $CH_2O + H_2O + Cu$ [30]. Theoretical calculations using B3LYP/6-31G [37, 38] along with Lanl2DZ pseudo-potentials on copper [39–41] were performed using the Gaussian 03 package [42]; it was found that the reaction takes place following a stepwise mechanism where the first step is characterized by the copper reduction ($Cu^{2+} \rightarrow Cu^+$) that activates an oxygen transposition process; in the second step, a new copper reduction ($Cu^+ \rightarrow Cu^0$) comes together with a proton transfer that produce formaldehyde and the release of a water molecule. Figure 2 shows the energy and reaction force profiles for this reaction. It can be observed that there are five reaction regions defined through the reaction force profile. These are the reactant (R) region; the transition state region (TS); the MSI region, where a metastable intermediate is observed; the QTS region, where a quasi-transition state was characterized; and the product region (P) where the system relaxes toward the products of the reaction [30]. Figure 3 displays the structure of the transition state and presents the partitioning of the supermolecule into three ionic fragments to which calculation of the reaction electronic flux were performed.

Figure 4 displays the REF decomposition in polarization and transfer contributions. It can be observed that the latter leads the electronic activity from the very beginning of the reaction. The effect of electronic transfer is quite marked within the transition state region, where a first reduction of
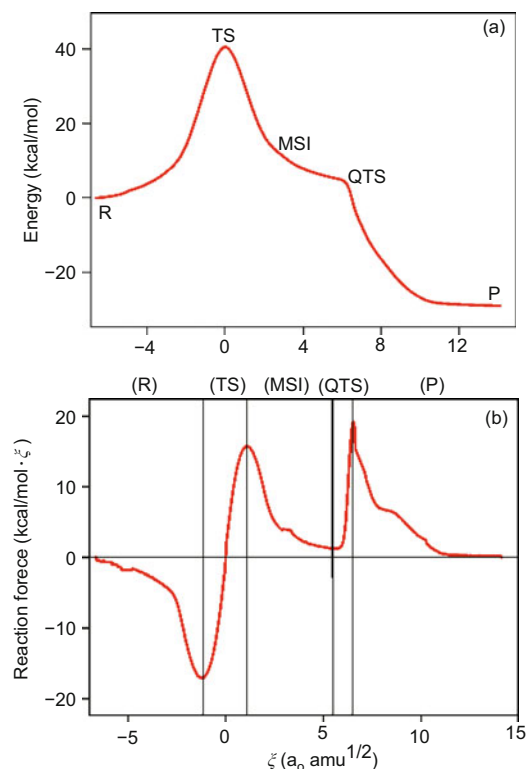

Figure 2 Energy (a) and reaction force (b) profiles for the methanol decomposition reaction.
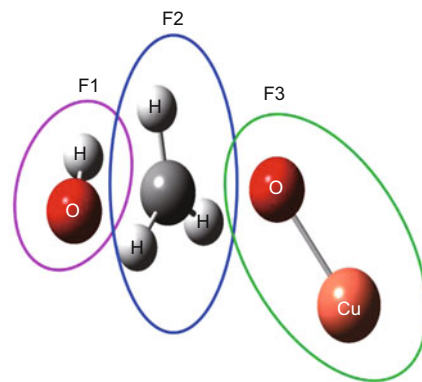

Figure 3 Molecular structure of the transition state and fragmentation scheme used in the calculation of reaction electronic flux in the methanol decomposition reaction.
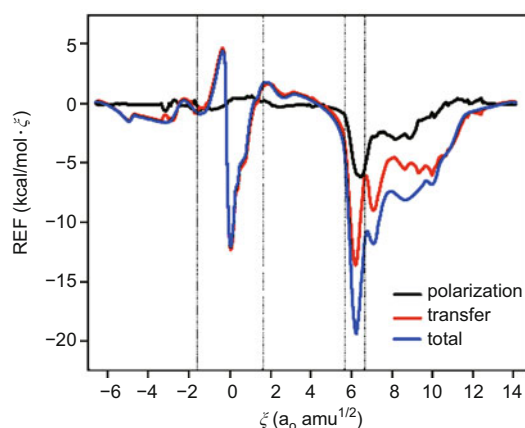

Figure 4 Decomposition of the reaction electronic flux in terms of polarization and transfer contributions in the methanol decomposition reaction.

the copper atom takes place. As the reaction continues within the quasi-transition state, the REF associated to transfer indicates that the second copper reduction is achieved; this leads to the formation of formaldehyde and the release of a water molecule. More details about the electronic activity taking place along this reaction can be obtained by analyzing the specific role of the fragments during the reaction.

Figure 5 displays the polarization and transfer fluxes per fragment. It can be observed in Figure 5(a) that fragments F1 and F3 are barely polarizable and most polarization effects take place on the methyl moiety F2. This latter shows a broad negative peak emerging at the QTS region, where it reaches its maximum intensity, then it spans practically the whole product region. This is the signature of a non-spontaneous

polarization effect that is most probably induced by the electron transfer taking place at earlier stages of the reaction, see Figure 5(b)

Figure 5(b) displays the transfer flux per fragment. It shows that all three moieties are quite active in electronic transfer although F3 leads the effect. This result is consistent with the mechanism involving successive reductions of the copper atom taking place along the reaction. On the other hand, it can be noticed that most electronic transfer occurs in a non-spontaneous fashion. This indicates that breaking processes, which are non-spontaneous events, control the course of the reaction.

4 Concluding remarks

We have presented the reaction electronic flux, $J(\xi)$, a new property that identifies and characterizes the electronic activity taking place during a chemical reaction. In this way it provides crucial and valuable information to characterize reaction mechanisms. The REF identifies the physical nature of the electronic activity by associating it to polarization and transfer effects. At the same time, the REF identifies the chemical fragments and specific chemical events that might be driving the reaction. The power of the REF as a descriptor to characterize the mechanism of chemical reactions has been illustrated with the analysis of two chemical processes. In the nucleophilic substitution reactions the REF showed that bond breaking or forming events may lead the electronic activity. In the catalytic decomposition of methanol by copper oxide, the REF showed that consecutive electronic reduction of copper together with bond breaking processes controls the course of the reaction.
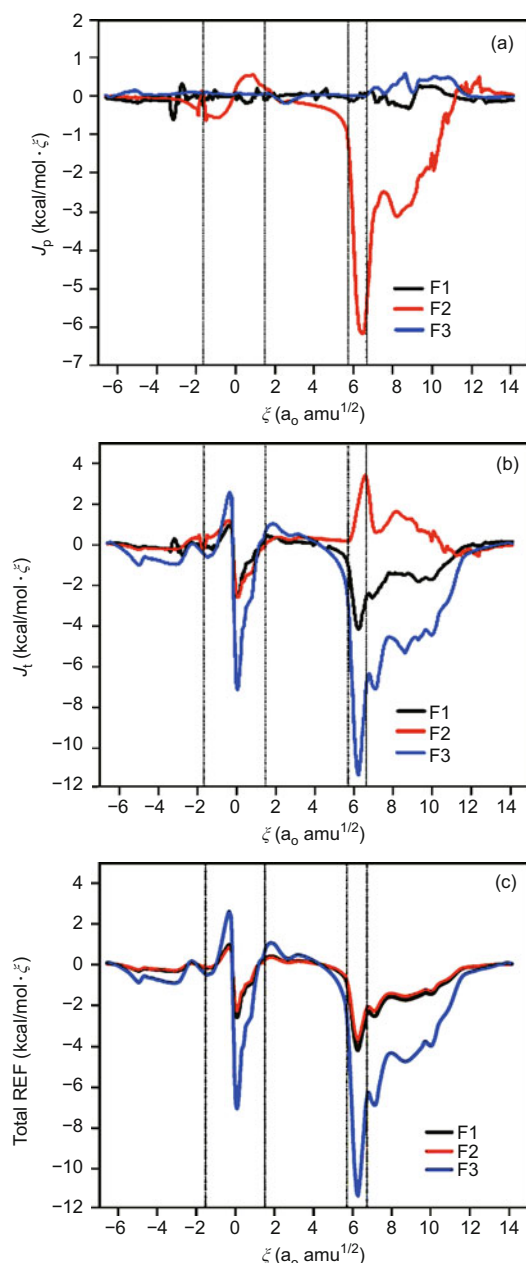
Figure 5 Fragment contributions to the polarization (a), transfer (b) and total electronic flux (c) in the methanol decomposition reaction.

1   Fukui K. A formulation of the reaction coordinate. *J Phys Chem*, 1970, 74: 4161–4163

2   Fukui K. The path of chemical reactions—The IRC approach. *Acc Chem Res*, 1981, 14: 363–368

3   Gonzalez C, Schlegel HB. An improved algorithm for reaction path following. *J Chem Phys*, 1989, 90: 2154–2161

4   Toro-Labbé A. Characterization of chemical reactions from the profiles of energy, chemical potential, and hardness. *J Phys Chem A*, 1999, 103: 4398–4403

5   Jaque P, Toro-Labbé A. Theoretical study of the double proton transfer in the CHX–XH···CHX–XH (X = O, S) complexes. *J Phys Chem A*, 2000, 104: 995–1003

6   Toro-Labbé A, Gutiérrez-Oliva S, Concha MC, Murray JS, Politzer P. Analysis of two intramolecular proton transfer processes in terms of the reaction force. *J Chem Phys*, 2004, 121: 4570–4576

7   Gutiérrez-Oliva S, Herrera B, Toro-Labbé A, Chermette H. The role of the reaction force to characterize the hydrogen transfer between sulfur and oxygen atoms. *J Phys Chem A*, 2005, 109: 1748–1751

8   Rincón E, Jaque P, Toro-Labbé A. Reaction force analysis of the effect of Mg(II) on the 1,3 intramolecular hydrogen transfer in thymine. *J Phys Chem A*, 2006, 110: 9478–9485

9   Toro-Labbé A, Gutiérrez-Oliva S, Murray JS, Politzer P. A new perspective on chemical and physical processes: The reaction force. *Molecul Phys*, 2007, 105: 2619–2625

10 Burda JV, Murray JS, Toro-Labbé A, Gutiérrez-Oliva S, Politzer P. Reaction force analysis of solvent effects in the addition of HCl to propene. *J Phys Chem A*, 2009, 113: 6500–6503

11 Toro-Labbé A, Gutiérrez-Oliva S, Murray JS, Politzer P. The reaction force and the transition region of a reaction. *J Mol Model*, 2009, 15: 707–710

12 Polanyi JC, Zewail AH. Direct observation of the transition state. *Acc Chem Res*, 1995, 28: 119–132

13 Zewail AH. Femtochemistry: Atomic-scale dynamics of the chemical bond. *J Phys Chem A*, 2000, 104: 5660–5694

14 Herrera B, Toro-Labbé A. The role of reaction force and chemical potential in characterizing the mechanism of double proton transfer in the adenine-uracil complex. *J Phys Chem A*, 2007, 111: 5921–5926

15 Echegaray E, Toro-Labbé A. Reaction electronic flux: A new concept to get insights into reaction mechanisms. Study of model symmetric nucleophilic substitutions. *J Phys Chem A*, 2008, 112: 11801–11807

16 Vogt-Geisse S, Toro-Labbé A. The mechanism of the interstellar isomerization reaction $HOC^+ \rightarrow HCO^+$ catalyzed by H_2: New insights from the reaction electronic flux. *J Chem Phys*, 2009, 130: 244308

17 Flores-Morales P, Gutiérrez-Oliva S, Silva E, Toro-Labbé A. The reaction electronic flux: A new descriptor of the electronic activity taking place during a chemical reaction. Application to the characterization of the mechanism of the Schiff's base formation in the Maillard reaction. *J Mol Struct (Theochem)*, 2010, 943: 121–126

18 Duarte F, Toro-Labbé A. The mechanism of H2 activation by (amino) carbenes. *J Phys Chem A*, 2011, 115: 3050–3059

19 Chermette H. Chemical reactivity indexes in Density Functional Theory. *J Comput Chem*, 1999, 20: 129–154

20 Geerlings P, De Proft F, Langenaeker W. Conceptual Density Functional Theory. *Chem Rev*, 2003, 103: 1793–1873

21 Pauling L. *The Nature of Chemical Bond*. New York: Cornell University Press, 1960

22 Sen KD, Jorgensen CK. *Electronegativity: Structure and Bonding*. Vol 66. Berlin: Springer Verlag, 1987

23 Parr RG, Yang W. *Density Functional Theory of Atoms and Molecules*. New York: Oxford University Press, 1989

24 Pearson RG. *Chemical Hardness*. Oxford: Wiley-VCH, 1997

25 Sanderson RT. Partial charges on atoms in organic compounds. *Science*, 1955, 121: 207–208

26 Sanderson RT. *Chemical Bonds and Bond Energy*. New York: Academic Press, 1976

27 Sengupta S, Toro-Labbé A. Estimating molecular electronic chemical potential and hardness from fragments' addition schemes. *J Phys Chem A*, 2002, 106: 4443–4446

28 Pearson RG. *Hard and Soft Acid and Bases*. Stroudsberg: Dowden, Hutchinson and Ross, 1973

29 Pearson RG. Absolute electronegativity and absolute hardness of Lewis acids and bases. *J Am Chem Soc*, 1985, 107: 6801–6806

30 Cerón ML, Herrera B, Araya P, Gracia F, Toro-Labbé A. The mechanism of methanol decomposition by CuO. A theoretical study based on the reaction force and reaction electronic flux analysis. *J Mol Model*, 2011, 17: 1625–1633

31 Boys S, Bernardi F. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Molec Phys*, 1970, 19: 553–566

32 Simón S, Durán M, Dannenberg JJ. How does basis set superposition error change the potential surfaces for hydrogen-bonded dimers? *J Chem Phys*, 1996, 105: 11024–11031

33 Burda JV, Toro-Labbé A, Gutiérrez-Oliva S, Murray JS, Politzer P. Decomposition of activation barriers to elucidate solvent effects. *J Phys Chem A*, 2007, 111: 2455–2457

34 Politzer P, Burda JV, Concha MC, Lane P, Murray JS. Analysis of the reaction force for a Gas phase S_N2 process: $CH_3Cl + H_2O \rightarrow CH_3OH + HCl$. *J Phys Chem A*, 2006, 110: 756–761

35 Ko JB, Bae CM, Jung YS, Kim DH. Cu-ZrO2 catalysts for water-gas-shift reaction at low temperatures. *Catal Letters*, 2005, 105: 157–161

36 Oguchi H, Kanai H, Utani K, Matsumura Y, Imamura S. Cu2O as active species in the steam reforming of methanol by CuO/ZrO$_2$ catalysts. *Appl Catal A Gral*, 2005, 293: 64-70

37 Becke AD. Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys*, 1993, 98: 5648–5652

38 Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B*, 1988, 37: 785–789

39 Hay PJ, Wadt WR. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J Chem Phys*, 1985, 82: 270–283

40 Hay PJ, Wadt WR. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. *J Chem Phys*, 1985, 82: 284–298

41 Hay PJ, Wadt WR. *Ab initio* effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J Chem Phys*, 1985, 82: 299–310

42 Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth G. A, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA. Gaussian 03, Revision D. 02. Pittsburgh: Gaussian, Inc., 2003

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