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Favorable Direction in a Chemical Reaction Through the Maximum Hardness Principle

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Abstract. Recently, an assessment regarding the validity of maximum hardness principle has been done taking 34 exothermic chemical reactions (Poater, J.; Swart, M.; Solà, M. *J. Mex. Chem. Soc.* **2012**, *56*, 311) in which only 46% and 53% of the total reactions have greater hardness for the products and the reactants than those for the reactants and the transition states, respectively. They have also mentioned that a larger set of reactions should be studied to draw a general conclusion regarding the validity of maximum hardness principle. We have noticed that the reactions having fewer number of reactants than that of products and / or very hard atoms like H, N, O, F or very hard molecules like H_2, N_2, HF, HCN, CH_4, etc. appearing in the reactant side, are more likely to disobey maximum hardness principle. In addition, dependence of hardness values on level of theory, basis sets, definitions, formulas, approximations should be kept in mind before criticising the validity of maximum hardness principle. Since these electronic structure principles are qualitative in nature, one should not expect them to be valid in all cases.
Key words: Maximum hardness principle, Hard-Soft Acid-Base (HSAB) principle, hardness, Koopmans' Theorem.

Resumen. Recientemente se realizó una validación del principio de máxima dureza en 34 reacciones químicas exotérmicas (Poater, J.; Swart, M.; Solà, M. *J. Mex. Chem. Soc.* **2012**, *56*, 311) en las que sólo 46% y 53% de las reacciones totales tiene mayor dureza para los productos y los reactivos que las de los reactivos y los estados de transición, respectivamente. También se menciona que se debe estudiar una serie más grande de reacciones para sacar una conclusión general sobre la validez del principio de máxima dureza. Hemos notado que las reacciones con un número menor de reactivos que de productos y/o átomos muy duros como H, N, O, F o moléculas muy duras como H_2, N_2, HF, HCN, CH_4, etc. que aparecen en el lado de los reactivos, son más propensas a desobedecer el principio de máxima dureza. Además, antes de criticar la validez del principio de máxima dureza se deben considerar la dependencia de los valores de dureza en el nivel de teoría, conjuntos de base, definiciones, fórmulasm y aproximaciones. Puesto que estos principios de estructura electrónica son de naturaleza cualitativa, no se debe esperar que sean válidos en todos los casos.
Palabras clave: Principio de máxima dureza, principio de ácidos y bases blandos y duros (HSAB), Teorema de Koopmans.

In a recent article [1], an assessment has been made of the validity of the maximum hardness principle (MHP) [2-5] in chemical reactions. The statement of Pearson's [2] MHP is, "there seems to be a rule of nature that molecules arrange themselves to be as hard as possible". The concept of hardness was first introduced by Pearson [6] through his famous hard-soft acid-base (HSAB) principle.

MHP has been found to be valid in the cases of molecular vibrations [7], internal rotations [8-12], chemical reactions [13], isomer stability [14], atomic shell structure [15,16], Woodward-Hoffmann rules [17,18], aromaticity [19-21], electronic excitations [22], time dependent situations [23], stability of magic clusters [24], chaotic ionizations [25] and several other categories of chemical processes [26-35] and there are also certain cases like a class of non-totally symmetric vibrations [36-41] and some chemical reactions [42-48] where it fails. Although it does not follow directly from the MHP, a corollary to it is proposed [27] suggesting the minimum hardness value at the transition state. Conditions under which that would be valid have been analyzed through symmetry considerations [49,50].

For an N- electron system with total energy E, the hardness is defined as

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\mathbf{r})} \tag{1}$$

where $v(\mathbf{r})$ is the external potential.

A finite difference approximation to eq (1) gives,

$$\eta = (I - A) \tag{2}$$

where I and A are the ionization potential and electron affinity, respectively. Further use of Koopmans' theorem [51] provides

$$\eta = (E_{LUMO} - E_{HOMO}) \tag{3}$$

where E_{HOMO} and E_{LUMO} stand for the energies of the highest occupied and the lowest unoccupied molecular orbitals, respectively. It may be noted that eqs (2) and (3) may provide qualitatively different trends in some cases.

In case there are two reactants / products in a reaction, a combined hardness [52] has been defined as

$$\eta = (I_{\min} - A_{\max}) \tag{4}$$

where $I_{\min}$ is the minimum of the two I- values and $A_{\max}$ is the maximum of the two A- values. A Koopmans' approximated version of this definition is used in reference [1]. It may be noted that sometimes both $I_{\min}$ and $A_{\max}$ belong to the same reactant / product and that provides a wrong trend. Arithmetic / geometric means have also been tried [53,54]. Poater *et al*. [1] have prescribed the use of the reactions where the chemical potential does not change significantly. They also prescribed that several reactions should be studied to have a general conclu-

sion. We have noticed that the reactions in which the number of reactants is more than that of products and/or very hard atoms like H, N, O, F or very hard molecules like H_2, N_2, HF, HCN, CH_4, etc. are present in the reactant side, the MHP is likely to fail. As most of the electronic structure principles are qualitative in nature, they are not expected to be valid in all cases. They do, however, provide us with a useful guide in many cases. Based on the suggestion made by Poater *et al*. [1], we are carrying out a thorough study to analyze the situations where the MHP will work and also the reactions where it is likely to fail. Effects of different sets of reactions, level of theory, basis sets, definitions, formulas, approximations, etc. on the validity of the MHP are being explored.

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