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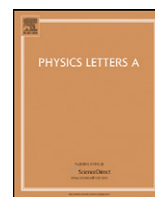


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## Phenomenological description of selected elementary chemical reaction mechanisms: An information-theoretic study

R.O. Esquivel<sup>a,b,d,\*</sup>, N. Flores-Gallegos<sup>a</sup>, C. Iuga<sup>a</sup>, E.M. Carrera<sup>a</sup>, J.C. Angulo<sup>b,d</sup>, J. Antolín<sup>c,d</sup>

<sup>a</sup> Departamento de Química, Universidad Autónoma Metropolitana, 09340 México D.F., Mexico

<sup>b</sup> Departamento de Física Atómica, Molecular y Nuclear, Universidad de Granada, 18071-Granada, Spain

<sup>c</sup> Departamento de Física Aplicada, EUITZ, Universidad de Zaragoza, 50018-Zaragoza, Spain

<sup>d</sup> Instituto Carlos I de Física Teórica y Computacional, Universidad de Granada, 18071-Granada, Spain

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### ABSTRACT

The information-theoretic description of the course of two elementary chemical reactions allows a phenomenological description of the chemical course of the hydrogenic abstraction and the  $S_N2$  identity reactions by use of Shannon entropic measures in position and momentum spaces. The analyses reveal their synchronous/asynchronous mechanistic behavior.

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### 1. Introduction

A reaction mechanism represents a sequence of elementary steps by which overall chemical change occurs, describing in detail what it takes place at each stage of a chemical transformation, such as the bonds that are being formed or broken, and in what order. The chemical course of a reaction also accounts for the order in which molecules react, either by single- or multi-step conversions, and provides information about the structure of the transition state (TS), reactive complexes, kinetics, catalysis, and stereochemistry. In this communication we present a theoretical *ab initio* study which presents evidence obtained from Shannon theoretic-information concepts in position and momentum spaces that allow a conceptual description of the course of two elementary chemical reactions, revealing all the expected physical transformations predicted for synchronous (one-step) and non-synchronous (two-step) reaction mechanisms.

Theoretical chemistry has witnessed a great deal of research to study the energetic of chemical reactions [1]. For instance, a variety of calculations of potential energy surfaces have been performed at various levels of sophistication [2]. Within the broad scope of these investigations, particular interest has been focused on extracting information about the stationary points of the en-

ergy surface. In spite of the fact that minima, maxima and the saddle point represent useful mathematical features to follow the reaction path of the energy hypersurface [3], it has been difficult to attribute too much chemical or physical meaning to these critical points though [4]. Whereas the reaction rate and the reaction barrier are chemical concepts which have been rigorously defined and experimentally studied since the early days of the transition state theory [5,6], the structure of the TS remains as a quest of physical organic chemistry. Understanding the TS is a fundamental goal of chemical reactivity theories which implies the knowledge of the chemical events that take place to better understand the kinetics and the dynamics of a reaction. On the other hand, a variety of density descriptors have been employed to study chemical reactions [7]. Particularly relevant is the reaction force analysis of a system's potential energy along the reaction coordinate which has been employed to characterize changes in the structural and/or electronic properties of chemical reactions [8].

Dewar [9] has employed intuitive arguments along with numerical evidence to put forward the notion of "synchronicity being normally prohibited for multibond processes", which is in contrast with the widely accepted Woodward–Hoffman rules [10] that establish that multibond "allowed" reactions must be synchronous, i.e., all the bond-forming and bond-breaking processes taking place simultaneously. Furthermore, it has been asserted [11] that a principle for non-perfect synchronization might be derived from the realization that the majority of elementary reactions involve more than one concurrent molecular process such as bond

\* Corresponding author at: Departamento de Química, Universidad Autónoma Metropolitana, 09340 México D.F., Mexico.

E-mail address: [esquivel@xanum.uam.mx](mailto:esquivel@xanum.uam.mx) (R.O. Esquivel).

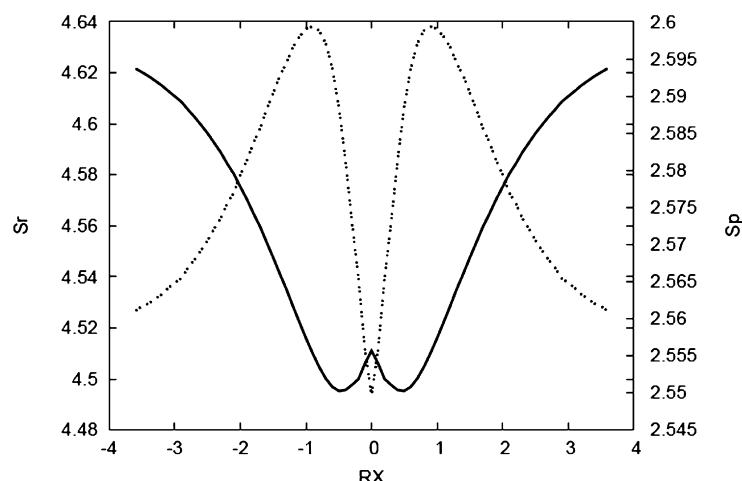


Fig. 1. Shannon entropies in position (solid line) and momentum (dashed line) spaces for the IRC path of the hydrogen abstraction reaction (A).

formation/cleavage, delocalization/localization of charge, etc., and that often these processes have made unequal progress at the transition state. For instance, one bond mechanisms are predominant in elementary processes of organic chemistry and most chemists believe these take place in a synchronous manner. Recently, the simplest prototypical hydrogen exchange reaction [12] and a variety of other radical exchange reactions have been examined [13] by use of *ab initio* methods to conclude that despite the fact that these reactions are chemically classified as being concerted (taking place in a single kinetic step) their bond-cleaving processes are slightly more advanced than the bond-forming ones, proceeding by a two-stage mechanism [9], and therefore they show asynchronous features.

There has been an increasing interest in the recent years to analyse the electronic structure of atoms and molecules by applying Information Theory (IT) [14–19]. These studies have shown that information-theoretic measures are capable of providing simple pictorial chemical descriptions of atoms and molecules and the processes they exert through the localized/delocalized behaviour of the electron densities in position and momentum spaces. In a recent study [20], we have provided with evidence which supports the utility of the theoretic-information measures in position and momentum spaces to detect the transition state and the stationary points of elementary chemical reactions so as to reveal the bond breaking/forming regions of the simplest hydrogen abstraction and the identity  $S_N2$  exchange chemical processes, thus providing evidence of the concept of a reaction having a continuum of transient of Zewail and Polanyi [29,30] and also in agreement with reaction force analysis [8].

The purpose of the present study is to follow the IRC path of the simplest hydrogen abstraction reaction  $H^\bullet + H_2 \rightarrow H_2 + H^\bullet$  and the exchange identity  $S_N2$  reaction  $H^- + CH_4 \rightarrow CH_4 + H^-$ , with the purpose of performing a phenomenological description of two selected elementary chemical reactions with different mechanistic courses by use of Shannon theoretic-information measures in both conjugated spaces, position and momentum.

## 2. Methods and discussion

The central quantities under study are the Shannon entropies in position and momentum spaces [21]:

$$S_r = - \int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d^3\mathbf{r} \quad (1)$$

and

$$S_p = - \int \gamma(\mathbf{p}) \ln \gamma(\mathbf{p}) d^3\mathbf{p} \quad (2)$$

where  $\rho(\mathbf{r})$  and  $\gamma(\mathbf{p})$  denote the molecular electronic distributions in the position and momentum spaces, each normalized to unity.

Abstraction reactions proceed by homolysis and can be characterized by a mechanism being kinetically of first order ( $S_N1$  like). These kind of reactions involve a *two-step mechanism*, which initiates with the formation of a new radical created by homolysis and continues with the recombination of the new radical with another radical species. Such homolytic bond cleavage occurs when the bond involved is non-polar and there is no electrophile or nucleophile at hand to promote heterolytic patterns. When the bond is made, the product has a lower energy than the reactants and it follows that breaking the bond requires energy. In contrast, the hydride-exchange reactions proceed by a  $S_N2$  mechanism which is characterized by being kinetically of second order (first order in each of the reactants: the nucleophile and the nucleofuge atoms). It has been postulated that the observed second order kinetics is the result of passage through the well-known Walden inversion transition state where the nucleophile displaces the nucleofuge (leaving group) from the backside in a single concerted reaction step.

The reaction  $H_a^\bullet + H_2 \rightarrow H_2 + H_b^\bullet$  is the simplest radical abstraction reaction involving a free radical,  $H_a^\bullet$  or  $H_b^\bullet$ , as a reactive intermediate (reaction A) whereas the  $H_a^- + CH_4 \rightarrow CH_4 + H_b^-$  is a typical  $S_N2$  identity exchange reaction (reaction B), where  $H_a^-$  represents the incoming nucleophile and  $H_b^-$  stands for the leaving nucleofuge. The electronic structure calculations performed in this study were carried out with the Gaussian 03 suite of programs [22]. The reported TS geometrical parameters for the abstraction [23], and the  $S_N2$  exchange reactions [24] were employed. Calculations for the structures of the internal reaction path were performed by use of the IRC method at the MP2/6-311++G\*\* (UMP2//6-311G for the abstraction reaction) level of theory. As a result of the latter, 72/93 points (chemical structures) evenly distributed on the forward and reverse directions of the IRC paths were obtained for the A/B reactions, respectively. Finally, a higher level of theory (QCISD(T)) and a properly balanced basis set (6-311++G\*\*) were chosen for both reactions to calculate the Shannon entropies of all chemical structures at the IRC paths. The molecular Shannon information entropies were obtained by employing software developed in our laboratory along with 3D numerical integration routines [25,26], and the DGRID suite of programs [27].

For reaction A (Fig. 1), both entropies possess richer structure at the vicinity of the TS as compared with the energy profile (which only shows one maximum at this point). By close inspection of Fig. 1, we note that the position entropy possesses a local

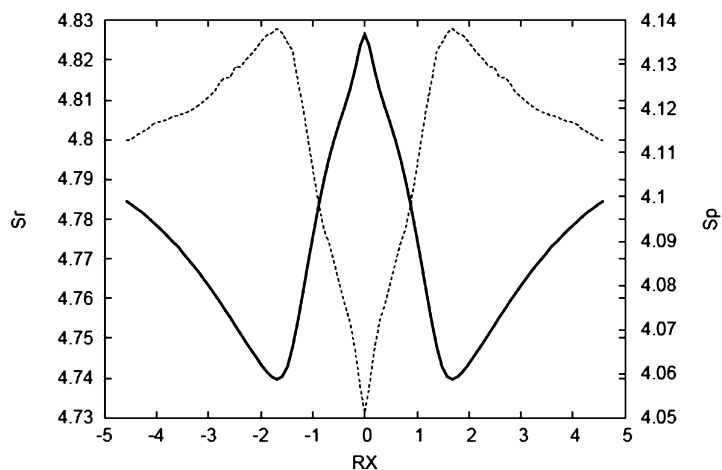


Fig. 2. Shannon entropies in position (solid line) and momentum (dashed line) spaces for the IRC path of the  $S_N2$  reaction (B).

maximum at the TS and two minima at its vicinity, whereas the momentum entropy decreases abruptly so as to reach a global minimum at the TS with two maxima at its vicinity.

The chemical picture proceeds in this way: as the intermediate radical ( $H_a^\bullet$ ) approaches the molecule at the TS region, the molecular density exerts important changes so as to undergo the homolysis. This represents a physical situation where the density in position space gets localized in preparation for the bond rupture, which in turn results in a local increase of the kinetic energy. This provides explanation for the well-known fact that bond breaking requires energy. Next, the bond is formed and as a consequence, the TS structure shows lower kinetic energy than the reactant/product complex ( $H_a^\bullet \cdots H-H_b$  or  $H_a-H \cdots H_b^\bullet$ ). Interestingly, from an information-theoretical perspective all of the above can be analogously described as observed in Fig. 1: as the radical intermediate approaches the TS region, the position entropies turn minimal when the position densities become localized and the corresponding momentum densities get delocalized (higher energies). Then at the TS, when the chemical structure relaxes, the position/momentum density gets delocalized/localized where the position/momentum entropy shows a local maximum/minimum. The process occurs in two steps in the way the reaction dictates, and this also might be observed from the theoretic-information context by closely examining the entropies behaviour at the proximity of the TS. That is, the bond breaking process requires energy which should in turn be dissipated by relaxing the structure at the TS, and we note from Fig. 1 that this is indeed the case in that maxima for the momentum entropy are located before minima of the position entropy (depending on the direction of the process), i.e., reactive complexes gain the necessary energy for bond cleavage at BCER (bond cleavage energy regions [20]) and then get localized as we described above. Next, the homolysis provokes energy/density relaxation of the molecules toward the TS which is also observed from the Shannon entropies as explained before.

For reaction B (Fig. 2), again both Shannon entropies show richer structure as compared to the total energy profile (which only possesses one maximum at the TS). By examining Fig. 2 we note that the position entropy profile features a maximum at the TS along with two minima at its vicinity, whereas the profile of the momentum entropy shows a global minimum at the TS with two maxima at its vicinity. It seems likely that these particular regions correspond with BCER where bond breaking is supposed to occur. It is interesting to note that for both entropies the BCER are located at the same IRC coordinate, in contrast with the two-stages mechanism of reaction A, and this may be indicative of the single step mechanism that characterizes the  $S_N2$  process, which highlights the localized/delocalized combination of the position/momentum

densities at this particular position of the IRP. At this point, it is interesting to associate the one step mechanism of this reaction to the chemical events that take place. While the nucleophile approaches the molecule the nucleofuge leaves it at unison, i.e., bond forming and bond breaking must occur in a concerted and synchronous manner. Both of these actions increase the energy of the combination: bond breaking requires energy (momentum density becomes delocalized and its corresponding entropy increases, and so its kinetic energy) as does overcoming the repulsion between the incoming ionic-complex (nucleophile) into close contact with the carbon's bonding shell (position density becomes localized and its corresponding entropy decreases). As the reaction process goes forward, the energy increases until a significant bonding begins to occur between the nucleophile and the molecule (increasing the position entropy and delocalizing its density). This releases enough energy to balance the energy required to break the carbon-nucleofuge bond (low kinetic energy structure with a highly localized momentum density). Then the transition state is reached.

It is worth mentioning that the abrupt changes apparently observed for the Shannon entropies in both reactions (Figs. 1 and 2) are largely due to the significant changes exerted by the densities at the vicinity of the TS within the BCER [20].

### 3. Conclusion

In this Letter we have shown that theoretic-information measures of the Shannon type possess the capability of revealing the hidden structure of the chemical reactions through phenomenological concepts [20] which permit to unveil the asynchronous/synchronous mechanistic behavior which characterizes reactions A and B, respectively. Furthermore, it is worth mentioning that the chemical phenomena treated here are largely invisible for most of the standard density descriptors, and certainly not accessible from the energy profile. We believe that this kind of studies may serve to provide with more specific information as to nourish chemical reactivity theories which pursue a full conceptual prediction of the TS structure from basic chemical principles [28]. On the other hand, it is our contention that these observations might be amenable of experimental verification through photodetachment techniques in the femtosecond time scale [29].

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