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Comparative study between a second derivative transition state search and a first derivative Hamilton-Jacobi minimum energy path

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Abstract

A comparative study between two different techniques to evaluate minimum energy paths has been carried out using three simple but representative reactions. Minimum energy paths obtained from a first derivative methodology (CARTE suit program) are similar to those found with an intrinsic reaction coordinate (IRC) methodology starting from geometries characterized by a second derivative methodology. The activation energies obtained from an extrapolated curve of the first derivative minimum reaction paths showed relative errors < 5 % with respect to the calculated by second derivative technique (Hessian matrix). Different optimization cycles and image numbers were used in the first derivative methodology to explore how these affect the minimum energy paths. For all the reactions studied, 25 optimization cycles were sufficient to reach a converged minimum reaction path and it was checked that in general, the use of 8 or 16 image numbers do not affect the minimum energy path behavior. We have showed how activation energies obtained from a first derivative Hamilton-Jacobi minimum energy path by a simple interpolation of an adjusted curve are in good agreement with the calculated from a second derivative methodology.

Keywords: MEP, Hamilton-Jacobi, QST, String, activation energy.

Estudio comparativo entre un buscador de estados de transición que usa segundas derivadas y un optimizador de caminos de mínima energía que usa primeras derivadas Hamilton-Jacobi

Resumen

Un estudio comparativo entre dos técnicas diferentes para evaluar caminos de mínima energía ha sido llevado a cabo usando tres simples pero representativas reacciones. Los caminos de mínima energía obtenidos a partir de un método que usa primeras derivadas (programa CARTE) son similares a aquellos obtenidos con una metodología de coordenadas de reacción intrínseca (IRC, por su siglas en inglés) partiendo de geometrías caracterizadas por un método que usa segundas derivadas. Las energías de activación obtenidas a partir de una curva extra-

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polada de los valores obtenidos a partir del método de primeras derivadas, mostraron errores relativos < 5% con respecto a las energías obtenidas con la técnica de segundas derivadas (Matriz Hessiana). Se utilizaron diferentes ciclos de optimización y número de imágenes con la finalidad de determinar cómo afectan estos a los caminos de mínima energía. Para todas las reacciones estudiadas, 25 ciclos de optimización fueron suficientes para alcanzar la convergencia de los caminos de mínima energía y se comprobó que en general el uso de 8 o 16 imágenes no afecta el comportamiento de los caminos de mínima energía. Hemos mostrado como las energías de activación obtenidas mediante la interpolación de una curva ajustada de caminos de reacción obtenidos a partir de un método de primeras derivadas Hamilton-Jacobi ofrecen resultados similares a los obtenidos a partir de una metodología de segundas derivadas.

Palabras clave: MEP, Hamilton-Jacobi, QST, string, energía de activación.

Introduction

With the aim of characterize reaction paths and transition states (TSs), computational methods for calculating minimum energy paths (MEPs) have been developed and applied for describing reaction mechanisms (1-5). In practice, only two strategies are used for MEPs calculations. In the first one, the TS is known and following the gradient of the energy downhill, both forward and backward, it is possible to map the MEP (5-7). In the second strategy, knowing the starting (reactants) and ending (products) points, a sample path is extrapolated and improved until reach the MEP (8, 9). In both strategies, many problems can be found for determining the MEP. For example, TS could not connect necessarily reactants and products if a poor potential energy surface (PES) is used or if not adequate reaction coordinate is implemented. On the other hand, identification of a TS starting from two minimums on the PES is not an easy task due to the high dimensionality of the surface. Thus, one question arises, which methodology is adequate to evaluate a MEP independently if products, reactants or TS are known.

Synchronous-transit has been extensively used for determining reaction paths and locating molecular transition states (4, 10-15). Linear (LST) and quadratic (QST) synchronous-transit use a linear or curve path between reactants and products, re-

spectively. The tangent to the path is used to choose the best eigenvector for the ascent direction and an eigenvector-following or quasi-Newton method is used to complete the optimization. Quasi-Newton methods are very efficient for minimization, but for locating TS (or saddle points), the convergence is very poor (16, 17). In recent years, the interest on methodologies that directly map MEPs using only potentials energies and first derivatives has increased such as the string method (8, 18-22). This method is an efficient numerical method which is based in a Hamilton-Jacobi type equation (23). In this method, a high order numerical scheme is constructed to estimate the first order spatial derivatives, or the tangent vectors. It is very important to point out that, despite the goodness of MEP obtained from the method, no information is available of the TS geometry because geometries obtained from the MEP do not necessarily correspond to the TS geometry. TS geometries are obtained by optimization processes of saddle points starting from geometries close to the highest point of the optimized MEP. Recently, an implementation of the string method has been developed by the chemistry laboratory of the ENS Lyon (CARTE suite) (24). The program is independent and calls external programs to obtain the energies and forces for the path optimization. The originality of this program lies in the set of coordinates that it can use to generate and to optimize the path.

Whatever the methodology used, the TS searching is computationally demanding but necessary to estimate the activation energy unless some approximation to the TS energy can be obtained. Then, with the aim of determine if similar MEPs can be obtained from a first derivative method and with a conventional second derivative method, three reactions are studied in this work. For this, MEPs from the CARTE suit program are compared with the quadratic synchronous-transit (QST2 or QST3) method of the Gaussian 03 package (25). In all QST calculations, IRC was used to verify the reaction path connecting reactants, TSS and products (26). In this work, we show that estimating first derivative MEP, very closer activation energies can be obtained with respect to the calculated with a second derivative method.

Theoretical aspects

All calculations were performed with the Gaussian 03 program in the context of density functional theory (DFT). For the string method, Gaussian 03 was used as external program to calculate energies and forces. The Becke's three parameters hybrid functional with Lee, Yang and Parr correlation functional and the 6-31G(d, p) basis set were employed (27-29). This methodology has showed to be very efficiently to evaluate activation energies of some gas phase reactions (13, 30, 31).

Two schemes were developed to calculate the MEP. Scheme A, employs the quasi-Newton method. Transition state geometries are obtained from QST2 or QST3 calculations followed by a tight optimization of the TS to improve the numerical values of the Hessian matrix. Frequency calculations are performed to characterize the nature of the stationary points on the energy potential surface and IRC calculations to verify the connection between minimums and TS. Activation energies are calculated by the total energy (without any thermal contribution)

difference between TS and reactants. In the scheme B, the CARTE suit program creates a set of images between optimized reactants and products (equidistant in the reaction coordinate) that are optimized. Different number of images and optimization cycles are studied in order to know how these parameters change the MEP. The maximum step length during path optimization was set to 0.04 a.u. for all calculations. Despite different equations can be employed to adjust the MEP obtained from the string method (e.g. Gaussian equation), due its profile the optimized reaction paths (images obtained from the CARTE suit program) are adjusted by a polynomial equation

$$y = y_0 + \sum_i^5 b_i x^i \quad (1)$$

where y_0 , b_i , and x^i are constants which have been adjusted to the best fit of the curve. The best values of the extrapolated curve are obtained minimizing the chi-square (χ^2) value by a Levenberg-Marquardt algorithm (32, 33)

$$\chi^2 = \sum_i (y_i - f(x_i))^2 \quad (2)$$

where y_i and $f(x_i)$ are the string and adjusted curve points. The optimization process was stopped when $\Delta\chi^2 \leq 1 \times 10^{-9}$. The goodness of fit was evaluated by R^2 (coefficient of determination) which is computed as

$$R^2 = 1 - \frac{RSS}{TSS} \quad (3)$$

here RSS and TSS are the residual and total sum of squares, respectively. The activation energy is calculated by the difference between an extrapolated TS energy (point that corresponds to the maximum of the function) and reactants. In all the cases, MEPs are built using the relative total energy with

respect to the reactants. Relative activation energy errors are estimated using the following equation

$$\%error = \left| \frac{E_a^{IRC} - E_a^{STR}}{E_a^{IRC}} \right| \times 100 \quad (4)$$

where E_a^{IRC} and E_a^{STR} are the activation energies obtained from the IRC and string method, respectively.

Results and discussion

Figure 1 shows a schematic representation of the three reactions studied. Reaction (A) involves a S_N2 substitution where a chloride anion substitutes a bromide anion. In reactants and products, Cl^- and Br^- are fixed from the carbon atom at 3.0 and 3.2 Å respectively, in a perpendicular position with respect to the plane formed for the three hydrogen atoms. Reaction (B) is a rotational isomerization process passing through a trans conformational TS. Reaction (C) is the internal isomerization of HCN to CNH.

The calculated activation energies obtained using scheme A were 8.02, 1.08 and 52.66 mH for the reactions A, B and C, in that order. These values will be used as the exact activation energy for comparison with those obtained from the string method (scheme B). Figure 2 shows the MEPs performed at 10, 25 and 40 optimization cycles for the reaction A using the string method and 8 image number. It can be seen from the figure that 10 cycles are enough to optimize the MEP. The activation energy obtained with 10, 25 and 40 cycles are 7.77, 7.78 and 7.78 mH respectively, which indicates a relative error < 4% with respect to the 8.02 value. In order to determine if the number of images modifies the MEP behavior, a MEP optimization with 16 images and 25 optimization cycles was carried out for reaction A. The results show that, there is no appreciable difference between the MEPs optimized at 25 cycles with 16 and 8 images (see fig-

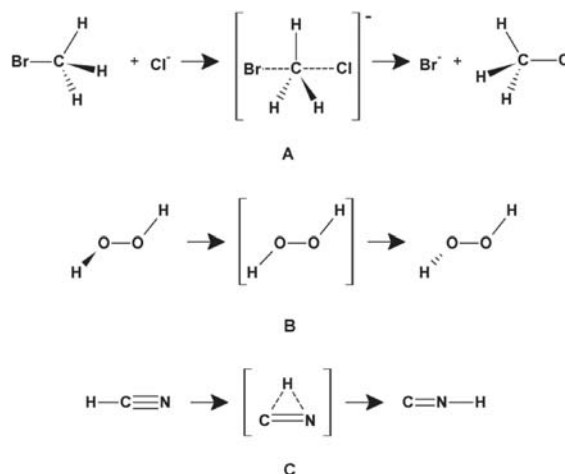


Figure 1. Schematic representation of the three reactions studied. A) S_N2 reaction of methyl-bromide with chloride anion, B) Rotational isomerization process H_2O_2 , C) Internal isomerization of HCN to CNH.

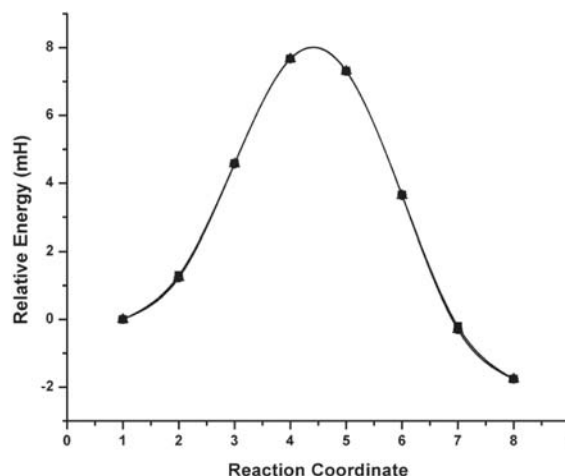


Figure 2. MEPs performed with 10, 25 and 40 optimization cycles for the S_N2 reaction of chloride and bromide anions (reaction A). ■ 10 cycles, ● 25 cycles and ▲ 40 cycles.

ure 3). The calculated activation energy for the MEP optimized with 16 images and 25 optimization cycles is 7.76 mH which is in good agreement with the values obtained with 8 images. In all cases, R^2 value was higher than 0.99 indicating the good fitting despite the lower number of images used.

For the rotational isomerization process (reaction B), 10 cycles are not enough to reach an optimum reaction path using 8 image number (see figure 4). This is due to the fact that the linear interpolation made by the CARTE suit program cannot produce an optimal set of images to connect reactants and products for a rotational isomerization. Consequently, this implies that more optimization cycles are needed to reach an adequate MEP. After 25 cycles, the MEP is completely optimized as indicates the overlapping with the 40 cycles curve. The calculated activation energy for the 25 and 40 optimization cycles were 1.09 and 1.08 mH respectively, with relative error < 1% in both cases. As in the case of the reaction A, a larger number of images do not affect the MEP behavior. The calculated activation energy using 16 images and 25 optimization cycles (1.09 mH) is

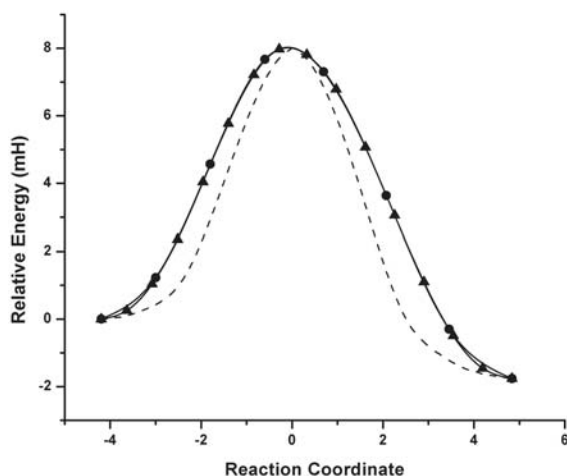


Figure 3. IRC and MEPs optimized with 25 cycles for the S_N2 reaction of chloride and bromide anions (reaction A). (---) IRC, ● 8 images and ▲ 16 images.

equal to the value obtained with 8 images and 25 optimization cycles. In general, the calculations performed with scheme B showed R^2 values around 0.99 indicative of an excellent fitting.

Pathway calculation for the reaction C, despite its apparent simplicity, is a little more complex. QST2 methodology fails to evaluate the saddle point structure because of a linear extrapolated structure to build the quadratic pathway between react and product is used (6). This leads to a structure with an H atom in the middle of the N-C bond making very difficult to find the saddle point structure. Hence, QST3 methodology using an initial structure for the TS was employed for this reaction. In the arbitrary initial guess of the TS, a H atom was collocated at 1.2 Å in a perpendicular distance to the center of the N-C bond (1.18 Å). With this initial guess, convergence is reached after 7 optimization cycles and the new structure was re-optimized as was mentioned in the theoretical aspects. As in the case of the scheme B, internal coordinates were employed to avoid the problem due to the lineal interpolation.

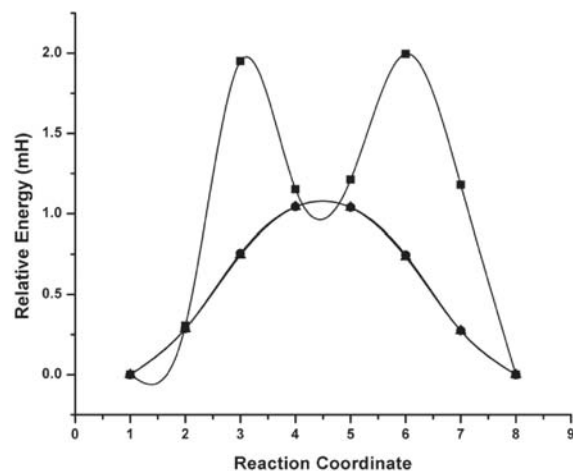


Figure 4. MEPs performed with 10, 25 and 40 optimization cycles for the rotational isomerization process (reaction B). ■ 10 cycles, ● 25 cycles and ▲ 40 cycles.

Figure 5 shows the MEPs corresponding to the reaction C optimized at 10, 25 and 40 cycles with 8 image number. As in the case of reaction B, 25 cycles are enough to achieve the convergence of the MEP. The calculated activation energies were 59.20, 50.34 and 49.95 mH for the 10, 25 and 40 optimization cycles, respectively. The relative errors were around 5% for the converged curves with R2 values higher than 0.98 indicative of good fitting in both cases.

As in the previous reaction studies, 16 images does not affect the behavior of the MEP (see figure 6). The calculated activation energy was 50.03 mH which shows a relative error of 5% as in the cases of the converged MEPs with 8 images. For all the cases, the R² was above 0.98 which demonstrate the excellent fitting of these MEPs.

Conclusions

As far we known, this is the first time that a comparison between extrapolated activation energies and direct TS-reactants energy difference is carried out. We have studied three simple but representative reactions (break and bond formation, rotational barrier and intramolecular hydrogen bond formation). Based in our results, it is possible estimates activation energies of simple reactions without a TS geometry. MEPs obtained with a first derivative methodology can be fitting to extrapolate the TS energy and avoiding the TS geometry calculation which is the more expensive part of the activation energy estimation. The activation energies obtained with the scheme B are in very good agreement with the values calculated using a TS characterized by one imaginary frequency of its Hessian matrix (scheme A).

For the CARTE suit program, 25 optimization cycles showed to be enough to reach convergence in the MEP at the maximum length of a step used (0.04 a.u.), independently of the image number used. On the other hand, the image number is not a determinant parameter in the MEP behavior at

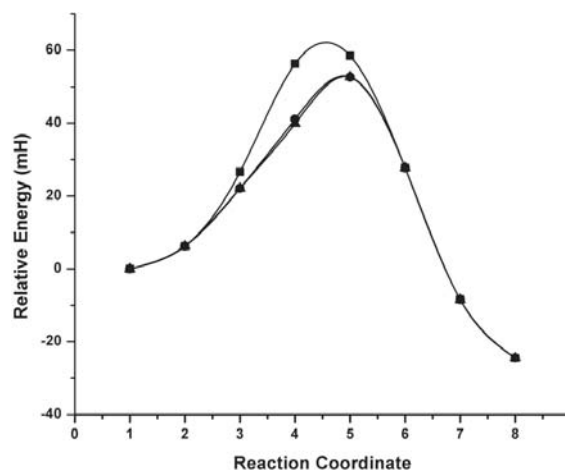


Figure 5. MEPs performed with 10, 25 and 40 optimization cycles for the internal isomerization of HCN to CNH (reaction C). ■ 10 cycles, ● 25 cycles and ▲ 40 cycles.

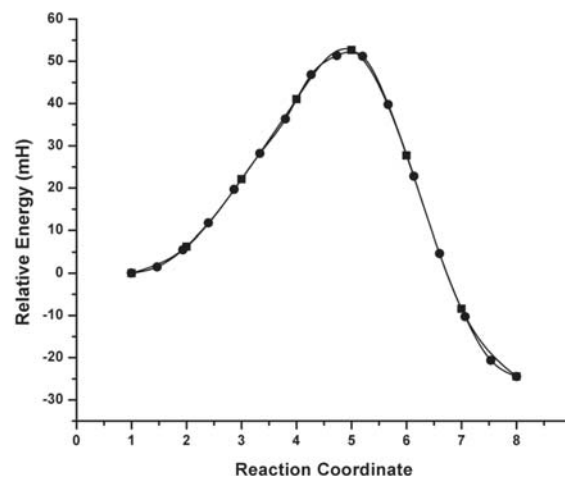


Figure 6. MEPs using 8 and 16 images at 25 optimization cycles for the internal isomerization of HCN to CNH (reaction C). ■ 8 images and ● 16 images. The reaction coordinate of the MEP optimized with 16 images was normalized to the 8 images.

least for the three reactions studied herein. Therefore, 8 images are enough to represent correctly the MEP using a first derivative Hamilton-Jacobi minimum energy path.

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