Development and Application of Fast Transition State-Finding Strategies for Catalyzed Reactions

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Introduction

Determination of transition states (TS) is important for understanding the kinetics of catalyzed reactions. Methods such as the nudged-elastic band (NEB) require an initial guess for the geometry of the TS and electronic structure calculations can fail if the guess is not correct. By contrast, the growing-string method (GSM) [1] requires only reactant and product geometries in order to initiate the search for the TS; however this method is computationally intensive because a large number of gradient calculations need to be made. Several modifications have been implemented in order to reduce the computational cost of the GSM, as well as the introduction of several TS-finding strategies. These improvements have been tested on four reactions of increasing complexity, showing a total reduction in computational time by a factor of 4-6.

Materials and Methods

Geometry optimizations for all reactant and product configurations were performed using QChem 3.0 with the B3LYP functional and 6-31G* basis sets for all atoms. The transition metals (V, Rh) were treated with the LANL2DZ basis set and effective core potential. All low-level force calculations were performed using HF and STO-3G basis sets. All high-level force calculations were performed using B3LYP and 6-31G* basis sets. The final TS estimate from a high-level string calculation was used to initiate a TS search in QChem at the B3LYP/6-31G* level of theory. The final converged TS for all examples was verified to have one negative Hessian eigenvalue.

Results and Discussion

Three important modifications were made to the GSM. First, internal coordinates were replaced by Cartesian coordinates because they are better able to describe the movement of atom(s) during elementary reactions. Second, the conjugate gradient method was replaced by the steepest descent method during the minimization of orthogonal forces in the search of points along the minimum energy path (MEP). Third, an interpolation scheme has been implemented to estimate the energy and gradient rather than using quantum mechanics (QM) code, thereby saving significant computational time. The interpolation scheme that was implemented was adopted from work previously done on reaction dynamics [2]. The modified-GSM was tested on four cases of increasing complexity: the Müller-Brown potential energy surface, alanine dipeptide isomerization, H-abstraction during methanol oxidation on isolated vanadate species supported on silica [3], and C-H bond activation in the oxidative carbonylation of toluene to *p*-toluic acid by Rh complexes [4]. The modified-GSM represents a 2-3 time reduction in computational effort relative to the original GSM [1], as measured by the number of QM gradients computed, without a sacrifice in the accuracy of the geometry and energy of the final TS.

Additional savings in computational effort were achieved by using several different TS-finding strategies: a hybrid method [5], an energy-weighted string, and a substring. The hybrid method was carried out by performing the initial search for the MEP at a lower level of theory, e.g. HF/STO-3G, and then refining the MEP using DFT at the B3LYP level with larger basis sets. The energy-weighted string places a higher density of points near where the energy is highest along the MEP, thereby giving finer resolution of the TS. Lastly, the substring strategy was employed in a similar manner as the hybrid method, except only a subset of the points on the final low-level string were refined at a higher level of theory. These available strategies have been tested on the same example reactions as mentioned above, further reducing the computational time to determine the TS by an additional factor of 2-3. Table 1 shows a summary of the computational time needed to determine the TS for each strategy for three of the reactions studied.

Table 1. Total CPU time to determine TS

Calculation Method*	Alanine Dipeptide	H-Transfer in VO_x/SiO_2	C-H Activation in Rh/TFA
Original GSM	130 h	1225 h	Did not converge
Modified-GSM	46 h	700 h	Did not converge
Modified-GSM, Hybrid Strategy	32 h	393 h	554 h
Modified-GSM, Energy-Weighting Strategy	20 h	334 h	--
Modified-GSM, Substring Strategy	16 h	256 h	--

*Total CPU time = CPU time for growing string + CPU time for optimizing TS estimate

Significance

The development of fast and accurate TS-finding strategies enables the determination of TSs for complex catalytic reactions promoted by homogenous or heterogeneous catalysts. Identifying kinetically relevant TSs is important for calculating rate constants and formulating reaction mechanisms.

References

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