



A reaction class approach with the integrated molecular orbital + molecular orbital methodology

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Abstract

We investigate the use of the reaction-class approach within the integrated molecular + molecular orbital (IMOMO) methodology for improving energetic information of chemical reactions. We have tested this approach using two classes of hydrogen abstraction reactions. One is abstraction from saturated hydrocarbons and the other from unsaturated hydrocarbons. For saturated hydrocarbon systems, this approach yields average unsigned errors of the order of 1 kcal/mol in the reaction energy and about 0.2 kcal/mol in the barrier height. The errors are larger in the unsaturated hydrocarbon systems and are of the order of 2 kcal/mol. Analysis of the performance shows that this approach provides a practical and cost-effective tool for studying reactions involving large molecules. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

An error of 2.0 kcal/mol in the barrier height gives a uncertainty factor of 29 to the thermal rate constant at the room temperature. Sometimes this is unacceptable. To achieve an error of less than 2.0 kcal/mol in the classical barrier height, one is required to employ a very accurate level of correlated molecular orbital (MO) theory currently available with a reasonably large basis set, e.g., the CCSD(T)/cc-pvtz level. Such calculations are computationally expensive for systems that have more than four non-hydrogen atoms. Furthermore, to obtain reasonably accurate kinetic properties, one is often required to go beyond the conventional transi-

tion-state theory. In such cases, one must provide much more potential energy information than just at the stationary points.

To circumvent this problem, particularly for large systems, one can employ the ONIOM approach proposed by Morokuma and co-workers [1–5]. This approach encompassing both the IMOMO and IMOMM models combines layers of different levels of MO theory and molecular-mechanics force fields to achieve an optimal cost/performance strategy in obtaining structural and energetic information. In this approach, a small sub-region of the whole system that is most critical to the chemistry is treated at an accurate level of theory and the remaining spectator region can be treated at a lower level in order to achieve computational efficiency. This approach has shown considerable promise so far [1–6]. Also within this framework, the correlated capped small sub-sys-

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tem (CCSS) method [7] attempts to include electron correlation only in the important small sub-system to achieve the same objective. One can think of this method as a specific selection of MO levels in the IMOMO strategy within the ONIOM approach. The results of the CCSS method are also encouraging [7–9]. An important note is that, in the ONIOM approach, the division of the whole system into sub-systems is left entirely to the chemical intuition of the user as well as the selection of levels of theory for different layers.

One particularly unique division is from our recently proposed reaction-class approach [10]. This approach was developed to achieve computational efficiency in predicting thermal rate constants of chemical reactions involving large molecules. The central idea is from recognizing that reactions that have the same reactive moiety have similar features on their potential energy surfaces along that particular reaction path direction. Thus, we can transfer certain potential information from the principal reaction (the smallest reaction in the class) to larger reactions in the same class without having to calculate it explicitly. Consequently, we can save an enormous amount of time and computational cost in developing detailed kinetic models. The central question here is that can we use the ONIOM methodology within the reaction-class approach as a way to improve energetic information along the minimum energy path (MEP). The reaction class offers a unique way to divide the system into layers of the IMOMO model. Thus, our main objective in this study is to investigate whether this IMOMO model would be sufficiently accurate in reproducing energy in the transition-state region from full calculations.

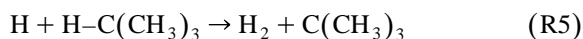
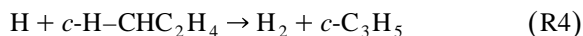
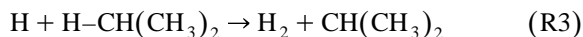
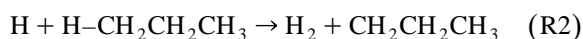
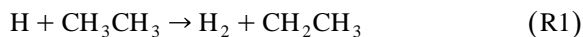
2. Theory and computational details

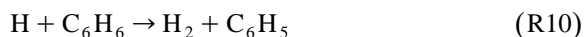
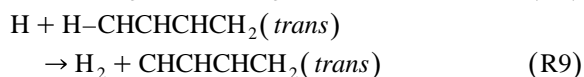
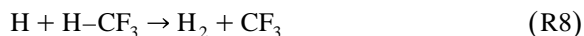
In this reaction-class model, the model system consists of only atoms in the reactive moiety, namely atoms whose nature of their chemical bonding was changed during the course of the reaction, and capped hydrogen atoms. This is the smallest model of the real system that is to be treated at a high level of theory. The remaining atoms in the system are treated at the low level in a two-layer IMOMO model. Due

to the use of capped hydrogen atoms to saturate valency of atoms in the boundary region between two layers, care must be taken to ensure the correct bonding characteristic of atoms in the reactive moiety for the unsaturated molecules. This often leads to the use of slightly larger model system as shown in test cases below.

As mentioned earlier, the selection of levels of theory is up to the user, depending on the application. Thus, certain restriction will apply on such a selection. Our interest is mainly in modeling gas-phase kinetics. In this case, the low level of theory is used to provide geometry, gradient and Hessian information along the MEP. This will require the low level to be sufficiently accurate so that single-point energies at the high level will not shift the location of the transition state far from the original one and make energy information out of synch with information calculated at the low level, particularly the generalized frequencies and the effective reduced mass in the multi-dimensional small-curvature tunneling formalism [11]. Such shifts would introduce unphysical errors in the rate calculations. From our experience, to avoid such errors the low level should be at least the second-order Møller–Plesset perturbation theory (MP2) or a non-local hybrid density functional theory (DFT).

We have selected two classes of hydrogen abstraction reactions. One class is the abstraction of hydrogen from saturated hydrocarbons that have classical barrier heights vary by 8 kcal/mol and reaction energies differ by more than 10 kcal/mol due to different substituents. The other class is hydrogen abstraction reactions from unsaturated and aromatic hydrocarbons. The relatively large number of test cases will provide a rather stringent test on the approach proposed here. In particular, these reactions are





Reactions R1–R8 have the same model system for high-level calculations, namely the $\text{H} + \text{HCH}_3$ reaction which is the principal reaction of this class. Reactions R1, R2 and R6 have only one capped hydrogen atom in their model system while reactions R3, R4 and R7 have two; reactions R5 and R8 have three. This selection also allows us to examine the effect of the number of capped hydrogen atoms in the model system on the calculated energetic properties of the real systems. Reactions R9 and R10 have the same model system, namely the $\text{H} + \text{H}_2\text{C}=\text{CH}_2$ reaction. Here we use the $=\text{CH}_2$ group to ensure the sp^2 carbon in the reactive moiety to have the same bonding characteristic in the model system. Note that resonance in aromatic and π -bond systems has very delocalized nature thus the use of small model system certainly will not be able to capture all of its electronic effects in the high level. Thus, we would expect the IMOMO methodology to have a larger error for R9 and R10.

Geometries of all reactants, products and transition states were fully optimized using the hybrid non-local Becke's Half-and-Half exchange [12] (as implemented in the GAUSSIAN98 program [13]) and Lee–Yang–Parr correlation [14] functionals denoted as B3LYP with the cc-pvDZ basis set. Previous studies [15,16] have shown that this hybrid non-local DFT method yields accurate transition-state geometries and frequencies of radical reactions. Thus, it is used as the low level in this study. MP4 is used as the high level with the cc-pvTZ basis set for all reactions except for R5 where cc-pvDZ was used due to the large computational demand in the MP4 calculations for the real system. In our previous studies, PMP4 was found to give accurate barrier heights for hydrogen abstraction reactions [17]. Thus, the IMOMO energy is given by

$$E(\text{IMOMO}) = E(\text{MP4/cc} - \text{pvTZ}; \text{model}) + \{ E(\text{B3LYP/cc} - \text{pvDZ}; \text{real}) - E(\text{B3LYP/cc} - \text{pvDZ}; \text{model}) \}. \quad (1)$$

Although we have used the MP4 theory as the high level in this study, the results obtained here should be general to other choice of high level of theory such as the QCISD or CCSD(T) level. All calculations were done using the GAUSSIAN98 program [13].

3. Results and discussion

Calculated MP4//B3LYP and IMOMO (MP4:B3LYP//B3LYP) reaction energies and classical barrier heights are listed in Table 1. Table 2 lists the same properties but calculated with the spin-projected PMP4 theory. There are several important results. First, the errors in the calculated reaction energy generally is larger than those in the barrier and such errors are larger in unsaturated π -bond and aromatic systems than in saturated hydrocarbons. In particular, for saturated hydrocarbon reactions (R1–R8), the average unsigned errors in the reaction energy are 0.98 kcal/mol for the IMOMO(MP4:B3LYP) and 1.08 kcal/mol for the IMOMO(PMP4:B3LYP) method whereas the corresponding errors in the barriers are 0.20 and 0.24 kcal/mol, respectively. Our results for the reaction energies are consistent with those of Coitiño et al. [7]. For unsaturated π -bond and aromatic systems R9–R10, the error in the reaction energy is of order 4–6 kcal/mol for the IMOMO(MP4:B3LYP) and 1–2 kcal/mol for the IMOMO(PMP4:B3LYP) method. The errors in the classical barrier are smaller than those in the reaction energy by less than 1 kcal/mol. The larger errors in the unsaturated hydrocarbon systems are expected due to the delocalized nature of the resonance effects as mentioned earlier. Second, the differences between MP4 and PMP4 results for the reaction energies and barriers (comparing the first and fourth columns in Tables 1 and 2) indicates that spin contamination in the HF wavefunction is rather noticeable, particularly for unsaturated hydrocarbon systems. However, for saturated hydrocarbon systems R1–R8 the similar magnitude of errors in the IMOMO model using either the MP4 or PMP4 level verifies that the spin contamination is rather localized in the reactive region so that the model system was able to account for most of its effect. This observation, however, is not true

Table 1

MP4/cc-pvtz and IMOMO (MP4/cc-pvtz:BHLYP/cc-pvdz) reaction energies, ΔE , classical barrier heights, ΔV^\ddagger , and errors $\Delta\Delta E_r$ ^a (kcal/mol)

Reactions	ΔE			ΔV^\ddagger		
	MP4	IMOMO	$\Delta\Delta E_r$	MP4	IMOMO	$\Delta\Delta E_r$
H + H-CH ₂ CH ₃	0.68	-0.17	0.85	13.64	13.73	-0.09
H + H-CH ₂ CH ₂ CH ₃	0.95	0.09	0.86	13.83	14.08	-0.25
H + H-CH(CH ₃) ₂	-1.72	-3.46	1.74	11.17	10.76	0.41
H + <i>c</i> -H-CHC ₂ H ₄	8.08	7.06	1.02	16.60	16.59	0.01
H + H-C(CH ₃) ₃ ^b	-2.08	-4.48	2.40	9.94	10.29	-0.35
H + H-CH ₂ F	-0.19	-0.66	0.47	14.52	14.30	0.22
H + H-CHF ₂	-0.01	-0.49	0.48	14.51	14.26	0.25
H + H-CF ₃	4.93	4.97	-0.04	17.50	17.49	0.01
H + H-CHCHCHCH ₂ ^b	22.69	18.63	4.06	31.11	26.66	4.45
H + C ₆ H ₆ ^b	27.13	20.99	6.14	34.47	29.03	5.44

^a Error = $\Delta\Delta E_r = \Delta E(\text{MP4}) - \Delta E(\text{IMOMO})$.

^b cc-pvdz was used in the MP4 calculations instead.

for unsaturated hydrocarbon systems where PMP4 method yields noticeable smaller errors. Third, there is no clear trend on the dependence of number of capped hydrogen atoms in the model system. For hydrocarbon reactions R1–R5, there appears an increase in the error in both the reaction energy and the barrier with increasing the number of capped hydrogen atoms. However, such a trend is not observed in the fluorohydrocarbon reactions R6–R8. Finally, the use of the IMOMO approach significantly reduces the computational cost as the system getting larger. For instance, the total CPU time re-

quired for computing the MP4 reaction energy and barrier for the H + benzene reaction (R10) is reduced by a factor of 57 with the use of the IMOMO approach.

For saturated hydrocarbon systems, the small errors for the barriers indicate that the IMOMO model can be used in improving energetic information along the MEP for rate calculations. This will greatly reduce the computational cost while introducing an error of less than 40% in the rate constants. This error is much less than one would expect for the uncertainty of selecting a level of theory for electron

Table 2

PMP4/cc-pvtz and IMOMO (PMP4/cc-pvtz: BHLYP/cc-pvdz) reaction energies, ΔE , and classical barrier heights, ΔV^\ddagger , and errors $\Delta\Delta E_r$ ^a (kcal/mol)

Reactions	ΔE			ΔV^\ddagger		
	PMP4	IMOMO	$\Delta\Delta E_r$	PMP4	IMOMO	$\Delta\Delta E_r$
H + H-CH ₂ CH ₃	-0.11	-0.87	0.76	11.75	11.79	-0.04
H + H-CH ₂ CH ₂ CH ₃	0.17	-0.61	0.78	11.94	12.15	-0.21
H + H-CH(CH ₃) ₂	-2.55	-4.15	2.60	9.32	8.61	0.74
H + <i>c</i> -H-CHC ₂ H ₄	7.41	6.43	0.98	14.81	14.76	0.05
H + H-C(CH ₃) ₃ ^b	-2.90	-5.13	2.23	8.20	8.55	-0.35
H + H-CH ₂ F	-0.87	-1.29	0.42	12.61	12.45	0.16
H + H-CHF ₂	-0.48	-1.04	0.56	12.58	12.43	0.15
H + H-CF ₃	4.61	4.38	0.23	15.49	15.63	-0.14
H + H-CHCHCHCH ₂ ^b	12.21	10.68	1.53	19.23	18.16	1.07
H + C ₆ H ₆ ^b	14.79	12.56	2.13	20.90	19.31	1.59

^a Error = $\Delta\Delta E_r = \Delta E(\text{PMP4}) - \Delta E(\text{IMOMO})$.

^b cc-pvdz was used in the PMP4 calculations instead.

correlation and basis set. For unsaturated hydrocarbon systems, care must be taken to minimize the spin contamination in the high level calculations.

4. Conclusion

In the present Letter, we have demonstrated the use of the reaction-class approach within the IMOMO methodology as a cost-effective way to improve energetic information in the transition-state region for thermal rate calculations. For saturated hydrocarbon systems, the average unsigned errors in the calculated barrier height of an order of 0.2 kcal/mol are much smaller than those of the reaction energies for a rather large class of hydrogen abstraction reactions. However, for unsaturated π -bond and aromatic systems, the errors of the IMOMO model in the reaction energy and barrier height are larger. Such errors are of the order of 2 kcal/mol when spin contamination in the wavefunction had been projected. With this level of accuracy, particularly for saturated hydrocarbons, one can combine the IMOMO model with the reaction-class approach to produce a powerful tool for predicting kinetics of large systems. Such study is being reported in a separated paper [18].

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