How Well Can Hybrid Density Functional Methods Predict Transition State Geometries and Barrier Heights?

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We compare hybrid Hartree−Fock density-functional theory to ab initio approaches for locating saddle point geometries and calculating barrier heights on a Born−Oppenhiemer potential energy surface. We located reactant, product, and saddle point stationary points for 22 reactions by the MP2 and QCISD ab initio methods and the B3LYP, BH&HLYP, mPW1PW91, and MPW1K hybrid Hartree−Fock DFT methods. We examined all of these methods with two basis sets, 6-31+G(d,p) and MG3. By comparison to calculations on five systems where the saddle point has been optimized at a high level of theory, we determined that the best saddle point geometries were obtained using the MPW1K and QCISD levels of theory. Of the methods tested, mPW1PW91 and B3LYP are the least effective for determining saddle point geometries and have mean unsigned error in barrier heights of 3.4−4.2 kcal/mol, depending on the basis set. In contrast, the MPW1K level of theory predicts the most accurate saddle point geometries and has a mean unsigned error of only 1.5 kcal/mol for either basis set. For even better accuracy, the combination of MPW1K/6-31+G(d,p) geometry calculations with QCISD(T)/MG3 or CCSD(T)/MG3 single-point energy calculations is shown to have an excellent performance-to-cost ratio. As a side product of this work, we report optimized scale factors for computing zero point energies by MPW1K.

1. Introduction

Hybrid Hartree−Fock density-functional theory (hereafter called hybrid DFT) is of great interest for computational thermochemistry and thermochemical kinetics. Its low computational cost compared to ab initio methods makes it a very attractive alternative for many applications. Although the good performance of hybrid DFT in structural and thermochemical applications is well documented, its usefulness in kinetics calculations has not been as well established. There are several varieties of hybrid DFT based on various mixing fractions and functionals; more recent density functionals show great promise for improvement in the calculation of reaction barrier heights and transition state geometries.

Hybrid DFT involves mixing various amounts of the Hartree−Fock (HF) nonlocal exchange operator with DFT exchange-correlation functionals. Two very promising hybrid DFT methods are B3LYP[1] and mPW1PW91.[2] These hybrid DFT methods have proven to be a successful approach to obtaining accurate molecular structures, vibrational frequencies, and bond energies. The most important parameter that varies in these methods is the fraction of HF exchange (set to 20% in B3LYP and 25% in mPW1PW91).

Although hybrid DFT is successful in predicting properties of stable molecules, it is a more challenging test to obtain accurate energies at an arbitrary point on a potential energy surface, especially points with partially formed bonds. It has been observed that the fraction of HF exchange one needs to accurately predict thermochemical properties differs from the optimal fraction to predict accurate barrier heights. For example, it has been shown empirically that the BH&HLYP[3] method gives more accurate barrier heights than B3LYP. The BH&HLYP method most significantly differs from B3LYP in that the HF exchange is set to 50%, but this significantly decreases the accuracy of calculated bond energies and energies of reaction at the same time that it improves calculated barrier heights.[4] Recently, we have parametrized a method that stands in relation to mPW1PW91 as BH&HLYP stands in relation to B3LYP, and we obtained much better performance for both kinetics calculations and bond energies. This is attributed to the improved long-range behavior of the modified Perdew-Wang density functional[2] used in mPW1PW91. The resulting method as we optimized it for kinetics is called modified Perdew−Wang 1-parameter-method for kinetics[4] (MPW1K).

Reaction-path calculations require energy gradients as well as single-point energies (i.e., energy values for a fixed geometry), and the efficient calculation of vibrational frequencies and characterization of stationary points as minima or saddle points requires Hessians (second derivatives of the energy with respect to nuclear coordinates). Geometry optimization (i.e., the location of stationary points on the potential energy surface) also requires gradients, and optimization of difficult structures such as saddle points often requires at least one Hessian. Furthermore, for fitting potential energy surfaces[5] and for direct dynamics calculations[6] (in which the need for a fit is circumvented by performing electronic structure calculations on the fly as needed by the dynamics algorithm), one requires a large number of energies and sometimes a large number of gradients and Hessians. Thus, a major issue in selecting electronic structure methods for dynamics applications is the performance-to-cost ratio, which may be gauged by considering the mean error for test data in relation to the typical computer resources required. With either explicitly correlated methods or DFT (either pure or hybrid), one must choose not only the method to treat correlation but also the one-electron basis set. The cost is a steep

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function of basis set size, and sometimes performance depends strongly on basis set as well.

The goal of the present paper is to study a variety of hybrid DFT methods to determine how accurately available hybrid DFT methods can predict saddle point geometries and reaction barrier heights with two good basis sets, how their performance depends on basis set size, and how much they cost compared to conventional ab initio methods. The paper extends ref 4 in that we consider saddle point geometries as well as barrier heights and energies of reaction, we systematically consider an augmented polarized valence triple-ζ basis set as well as an augmented polarized double-ζ basis set, and we have enlarged the database of test data. The cost consideration is dependent on system size but for quantitative estimations we will use a cost measure based primarily on a system with 11 atoms (2 carbons, 1 nitrogen, and 8 hydrogens). The conclusions clearly also depend on the test set; we will use a set of 22 reactions for which the true barrier height can be estimated reasonably reliably by comparing experimental data to dynamics calculations in the literature. These reactions mainly involve making and breaking single bonds in neutral molecules by the transfer of hydrogen, and so it is not as diverse a test set as one would like. However, even if the conclusions turn out to be valid only for reactions involving neutral atoms and rearrangements involving only single bonds or hydrogen transfers, their scope will encompass a large number of important applications. In a more qualitative way, though, the conclusions certainly apply as well to an even wider class of reactions, but it is beyond our scope or ability to quantify that here.

There has been extensive previous work on applications of DFT and hybrid DFT to transition states, and it is useful to place the present work in context. The situation up to 1995 is summarized by a symposium paper by Truong et al.,[7] who concluded from this work that “non-local DFT and hybrid DFT methods yield results of comparable accuracy to the second-order Møller−Plesset (MP2) method but at a much cheaper computational cost, especially for large systems.” This symposium volume also contains an overview by Baker et al.,[8] who, “drawing on a large body of recent work” concluded that hybrid DFT, in particular the Becke 3-parameter method based on the Perdew-Wang 1991 correlation functional (B3PW91), also called the adiabatic connection method (ACM), is “typically of better quality than MP2 and only marginally more expensive computationally than Hartree−Fock” for geometries, vibrational frequencies, energies, and barrier heights. In 1996 Durant[9] reported a systematic evaluation of one DFT method and four hybrid DFT methods including BH&HLYP, B3LYP, and B3PW91 for seven transition states. He found that the BH&HLYP hybrid DFT method was best for barrier heights, and he concluded that all functionals performed reasonably well for geometries. Jursic examined a variety of reactions and found that hybrid DFT methods, including B3LYP, generally underestimate the barrier height for abstraction of a hydrogen atom by a hydrogen atom.[10−12] A 1998 *Faraday Discussion* includes a summary[13] of what had been learned from 19 studies of the accuracy of various DFT and hybrid DFT methods for transition state geometries and barrier heights. It was concluded that “the B3PW91 and B3LYP methods, especially the latter, have yielded remarkably good accuracy for a number of applications to transition state geometries and energies. At the same time there are a number of cases where these methods are known to be quantitatively unreliable.” Some of the early conclusions about the accuracy of DFT and hybrid DFT methods suffer from the fact that calculations were compared to experimental Arrhenius activation energies rather than extracting a best estimate of the classical barrier height by detailed modeling of the observed rate constants in terms of a potential energy surface. The first attempt to create a reasonably large systematic database that did not have this deficiency was our own previous paper (with Fast and Harris),[4] where we created the first version of the database used here. With a 6-31+G(d,p) one-electron basis set, that paper found mean unsigned errors in barrier heights of 2.5, 4.8, 3.9, and 1.6 kcal/mol, respectively, for BH&HLYP, B3LYP, mPWPW91, and MPW1K. This study also indicated a systematic signed error in B3LYP and mPW1PW91 barrier heights, which tend to be too low. Kobayashi et al.[14] also found that B3LYP systematically underestimates barrier heights.

TABLE 1: Best Estimates of Classical Barrier Heights and Classical Endoergicity for the Reaction Set[a]

reaction	ΔE	$V_f^\ddagger$	$V_r^\ddagger$
1. $Cl + H_2 \rightarrow HC1 + H$	−3.1	8.7	5.6
2. $OH + H_2 \rightarrow H + H_2O$	−16.3	5.7	22.0
3. $CH_3 + H_2 \rightarrow H + CH_4$	−2.9	12.1	15.0
4. $OH + CH_4 \rightarrow CH_3 + H_2O$	−13.5	6.7	20.2
5. $H + CH_3OH \rightarrow CH_2OH + H_2$	−6.5	7.3	13.8
6. $H + H_2 \rightarrow H_2 + H$	0.0	9.6	9.6
7. $OH + NH_3 \rightarrow H_2O + NH_2$	−10.0	3.2	13.2
8. $HCl + CH_3 \rightarrow Cl + CH_4$	−6.0	1.8	7.8
9. $OH + C_2H_6 \rightarrow H_2O + C_2H_5$	−17.3	3.4	20.7
10. $F + H_2 \rightarrow H + HF$	−31.4	1.8	33.2
11. $OH + CH_3 \rightarrow O + CH_4$	−5.9	7.8	13.7
12. $H + PH_3 \rightarrow PH_2 + H_2$	−22.3	3.2	25.5
13. $H + ClH' \rightarrow HC1 + H'$	0.0	18.0	18.0
14. $OH + H \rightarrow H_2 + O$	−3.0	10.1	13.1
15. $H +$ *trans*-$N_2H_2 \rightarrow H_2 + N_2H$	−35.1	5.9	41.0
16. $H + H_2S \rightarrow H_2 + HS$	−13.8	3.6	17.4
17. $O + HCl \rightarrow OH + Cl$	−0.1	9.8	9.9
18. $CH_4 + NH \rightarrow NH_2 + CH_3$	−14.2	8.4	22.7
19. $C_2H_6 + NH \rightarrow NH_2 + C_2H_5$	−10.4	8.0	18.4
20. $C_2H_6 + NH_2 \rightarrow C_2H_5 + NH_3$	−7.4	10.4	17.8
21. $NH_2 + CH_4 \rightarrow CH_3 + NH_3$	−3.4	14.5	17.9
22. *s-trans cis*-$C_5H_8 \rightarrow$ *s-trans cis*-C_5H_8	0.0	38.4	38.4

[a] Units are kilocalories per mole.

Our previous findings[4] with a 6-31+G(d,p) basis raise the issue of basis set effects on DFT and hybrid DFT predictions. The original, perhaps naive, expectation of many workers was that basis set effects would be smaller on DFT calculations than on calculations involving explicitly correlated wave functions. Detailed studies of this effect bear out this expectation; nevertheless, large basis sets are often required for accurate results.[15−17] A finding in our own previous study,[4] employing mPW1PW91 and MPW1K, is the importance of diffuse functions in obtaining a balanced treatment of bond energies across a range of bond types. It seems that the lack of diffuse functions in the basis sets may contribute more significantly to the errors obtained in some applications than is widely appreciated. One of the goals of the present work is to systematically explore the effect of further increases in basis set size.

In addition to making a systematic study of basis set effects on hybrid DFT barrier heights, the present paper provides a first systematic attempt to evaluate the accuracy of predicted saddle point geometries.

Section 2 summarizes the test set. Section 3 summarizes all methods and basis sets to be tested. Section 4 presents results and discussion.

2. Databases

2.1. Energetics. The test set we will use in our comparisons consists of the 22 reactions listed in Table 1. All energies reported in this paper will be molar energies in units of kcal.

TABLE 2: Best Estimates of Saddle Point Geometries for A + BC → AB + C[a]

reaction A + BC	$R^{\ddagger}_{AB}$	$R^{\ddagger}_{BC}$	$R^{\ddagger}_{sum}$	$\theta^{\ddagger}_{ABC}$	ref
1. $Cl + H_2 \rightarrow HC1 + H$	0.981	1.431	2.412	180	12
6. $H + H_2 \rightarrow H_2 + H$	0.930	0.930	1.860	180	13
10. $F + H_2 \rightarrow H + HF$	1.546	0.771	2.317	119	14
13. $H + ClH' \rightarrow HC1 + H'$	1.480	1.480	2.960	180	12
14. $H + HO \rightarrow H_2 + O$	0.894	1.215	2.109	180	15

[a] Units are angstroms and degrees.

The table lists our best estimate of the zero-point exclusive endoergicity ΔE and forward (f) and reverse (r) barrier height $V^{\ddagger}_{x}$, which are related by

$$V^{\ddagger}_{f} = V^{\ddagger}_{r} + \Delta E \qquad (1)$$

Note that ΔE is also called the energy of reaction or classical endoergicity (it is negative for an exoergic reaction), and $V^{\ddagger}_{x}$ is also called classical barrier height. The best estimates of the classical endoergicities were obtained by removing the zero point contributions from experimental heats of formation at 0 K; in particular they were calculated from zero-point exclusive atomization energies that were obtained in this way.[18] The best estimate of the classical barrier heights for 20 of the reactions (1−20) comes from our previously published[4] best estimate of the barrier heights for these reactions and is explained in that previous paper. For reaction 21, $NH_2 + CH_4$, the best estimate of the barrier was determined from theoretical[19] and experimental[18,20] data using the method described previously.[4] For reaction 22, the [1,5] hydrogen shift isomerization of *cis*-1,3-pentadiene, the best estimate of the classical barrier height was obtained by a scheme similar to that used for the other reactions by basing the estimate on reaction rates for the [1,5] deuterium shift that had been calculated[21] on both AM1 and PM3 potential surfaces. The AM1 surface has a barrier height of 39.5 kcal/mol and underestimates the reaction rate; the PM3 surface predicts a barrier height of 36.6 kcal/mol and overestimates the reaction rate. The best estimate of $V^{\ddagger}$ was taken from a linear interpolation of the logarithm of the two calculated rate constants vs the barrier height for these methods in order to obtain a rate constant that agrees with the experimental[22] value at 478.45 K. This gives our best estimate of the barrier height to be 38.4 kcal/mol. Clearly, our barrier height database is not as accurate or reliable as the widely used databases for heats of formation and atomization energies of stable molecules. Nevertheless, we believe it is accurate enough to serve as a starting point for testing methods for calculating saddle point properties. We encourage other researchers to suggest improvements in the database in the future.

2.2. Saddle Point Geometries. We also made a database of saddle point geometries. These are more difficult to determine, so our test set is smaller (reactions 1, 6, 10, 13, and 14), and it consists of reactions where very high-level calculations of saddle point geometries are available. These test data for saddle point geometries are given in Table 2, along with the literature references[23−26] for the calculations on which the estimates are based. Note that $V^{\ddagger}_{sum}$ denotes the sum of the making and breaking bond distances; this is a measure of the looseness of the structure in a direction perpendicular to the reaction coordinate. We will call this sum the perpendicular looseness.

3. Methods

The methods used for geometry optimization include the hybrid density functionals MPW1K,[4] mPW1PW91,[2] B3LYP,[1] BH&HLYP,[3] and two ab initio methods: Møller−Plesset second-order perturbation theory[27] (MP2), and quadratic configuration interaction with single and double excitations[28] (QCISD). We also performed energy calculations with the QCISD(T)[28] and CCSD(T)[29] methods; these methods each include two quasiperturbative terms involving connected triple excitations, one analogous to a fourth-order term in the Møller−Plesset theory and one analogous to a fifth-order term.[30] The basis sets employed are the 6-31+G(d,p) basis[31] and the modified G3Large basis,[32] which is called MG3 here and in ref 33 but is also known as G3MP2Large.[34] The MG3 basis is identical to the older 6-311++G(2df,2p) basis for H and first row atoms (C, N, O, F), and it may be thought of as an improved 6-311+G(3d2f, 2df, 2p) basis for the second row (Si, P, S, Cl). The most significant improvement over older basis sets is probably the inclusion of tight d functions for the second row; for example, the exponents of the tightest *d* functions on P, S, and Cl are 2.2, 2.6, and 3.0, respectively. The importance of tight *d* functions for the second row was first emphasized by Bauschlicher and Partridge[15,35] and Martin and Uzan,[36] and experience in our research group is fully consistent with their conclusions. For the $Cl-H-CH_3$ transition state, the MG3 basis has 121 contracted functions formed from 182 primitive Gaussians, as compared to 62 and 118 respectively for 6-31+G(d,p). For the $H_2N-H-CH_2CH_3$ transition state, the MG3 basis has 182 functions contracted from 252 primitives, as compared to 97 and 152 for 6-31+G(d,p).

The most important relativistic effect for reaction dynamics with first and second row elements is spin−orbit coupling. In all of the calculations presented in this paper, the spin−orbit stabilization energy was added to all atoms and to selected open-shell molecules, as described previously.[37] The spin−orbit contributions were assumed to be negligible at all transition states.

All of the calculations presented in this paper were performed with the Gaussian98 program.[38] All calculations on open-shell systems use the spin-unrestricted formalism,[3] e.g., UMP2, UQCISD, UB3LYP, UMPW1K, etc. All saddle points were verified to be first order with a frequency calculation, with the exception of reactions 9, 19, 20, and 22 at the QCISD/MG3 level. For these four systems, the numerical Hessian would require an excessive amount of computing resources, but the structures are very similar to those confirmed at lower levels. The structures of all MPW1K and QCISD optimized saddle points are given in Supporting Information.

The cost function we use is designed to be an estimate of the cost of a saddle point geometry optimization. The actual number of energies, gradients, and Hessians required for an optimization varies greatly depending on the system, initial geometry, coordinate system, and optimization algorithm. Therefore, for we defined a standard cost (C) by

$$C = 10(E + G) + H \qquad (2)$$

where E is the CPU time to perform an energy calculation in minutes, G is the time to calculate a gradient, and H is the time to calculate a Hessian. All of the timed calculations were performed on a single 300 MHz R12000 processor on an Origin 2000 computer, and the value tabulated is the sum of the C functions for calculations on two of the saddle point structures, namely $ClHCH_3$ and $H_2NHC_2H_5$. For single-point calculations, $X//Y$, where the geometry is optimized at level Y and a single-point energy is calculated at level X, the standard cost function is defined as

$$C(X//Y) = C(Y) + E(X) \qquad (3)$$

TABLE 3: Mean Errors (Ångstroms) in Internuclear Distances at Saddle Point for Reactions 1, 6, 10, 13, and 14

		bond distance			perpendicular looseness			
method	basis	MSE[a]	MUE[b]	RMSE[c]	MSE[a]	MUE[b]	RMSE[c]	cost
BH&HLYP/	6-31+G(d,p)	−0.01	0.04	0.06	−0.01	0.04	0.06	2.4(2)[d]
MPW1K/	6-31+G(d,p)	0.00	0.02	0.03	−0.01	0.02	0.02	2.5(2)
MP2/	6-31+G(d,p)	−0.03	0.03	0.05	−0.05	0.05	0.07	2.6(2)
QCISD/	6-31+G(d,p)	−0.01	0.03	0.04	−0.02	0.03	0.04	1.9(4)
BH&HLYP/	MG3	−0.01	0.03	0.05	−0.02	0.04	0.05	1.6(3)
MPW1K/	MG3	−0.01	0.01	0.01	−0.01	0.02	0.02	1.6(3)
MP2/	MG3	−0.03	0.04	0.06	−0.07	0.07	0.08	3.3(3)
QCISD/	MG3	−0.01	0.02	0.03	−0.01	0.02	0.03	1.9(5)

[a] Mean signed error. [b] Mean unsigned error. [c] Root mean squared error. [d] Power of 10 in parentheses.

TABLE 4: Mean Errors (Ångstroms) in Internuclear Distances at Saddle Point for Reactions 1, 6, 13, and 14

		bond distance			perpendicular looseness			
method	basis	MSE[a]	MUE[b]	RMSE[c]	MSE[a]	MUE[b]	RMSE[c]	cost
B3LYP/	6-31+G(d,p)	0.03	0.07	0.12	0.07	0.07	0.11	2.4(2)[d]
BH&HLYP/	6-31+G(d,p)	0.01	0.04	0.06	0.02	0.03	0.04	2.4(2)
mPW1PW91/	6-31+G(d,p)	0.01	0.03	0.06	0.03	0.03	0.05	2.5(2)
MPW1K/	6-31+G(d,p)	0.00	0.02	0.03	0.00	0.02	0.02	2.5(2)
MP2/	6-31+G(d,p)	−0.01	0.02	0.02	−0.03	0.03	0.03	2.6(2)
QCISD/	6-31+G(d,p)	0.00	0.02	0.02	0.00	0.01	0.01	1.9(4)
B3LYP/	MG3	0.01	0.05	0.09	0.03	0.06	0.09	1.6(3)
BH&HLYP/	MG3	0.00	0.03	0.04	0.00	0.02	0.02	1.6(3)
mPW1PW91/	MG3	0.01	0.04	0.08	0.02	0.03	0.05	1.6(3)
MPW1K/	MG3	0.00	0.01	0.01	−0.01	0.02	0.02	1.6(3)
MP2/	MG3	−0.02	0.03	0.04	−0.05	0.05	0.06	3.3(3)
QCISD/	MG3	0.00	0.02	0.03	0.00	0.01	0.01	1.9(5)

[a] Mean signed error. [b] Mean unsigned error. [c] Root mean squared error. [d] Power of 10 in parentheses.

4. Results and Discussion

4.1. Saddle Point Geometries. Table 3 summarizes the mean errors in $R^{\ddagger}_{\mathrm{makingbond}}$, $R^{\ddagger}_{\mathrm{breakingbond}}$, and perpendicular looseness for the methods that predict a barrier for all five reactions in the saddle point geometry test set. Table 4 summarizes the same information for four of the five reactions, leaving out reaction 10, F + H_2, but including the methods B3LYP and mPW1PW91 in the comparisons. Reaction 10 was left out of Table 4 because the B3LYP and mPW1PW91 methods predict that there is a monotonically downhill reaction path; thus they predict that the highest-energy point on the lowest-energy path is at reactants where $R^{\ddagger}_{\mathrm{makingbond}}$ is ∞. The errors in Tables 3 and 4 were computed using the values in Table 2 rounded to 0.001 Å along with the unrounded results of our calculations, but the mean errors are rounded to 0.01 Å to allow the significant trends to be seen more easily.

When all five reactions are considered, the lowest RMS error in bond distances for each of the two basis sets was achieved by MPW1K for both the 6-31+G(d,p), and MG3 basis sets. In Table 4 where the B3LYP and mPW1PW91 methods are considered, they have the highest RMS error in bond distances, even though the case on which they do worst is omitted. It can be seen that B3LYP and mPW1PW91 methods predict looser saddle points in the perpendicular direction. That is, they tend to overestimate the sum of the bond distances for the forming and breaking bonds at the saddle point. MP2 has the opposite trend for perpendicular looseness. The methods BH&HLYP, MPW1K, and QCISD do not exhibit a systematic error in perpendicular looseness as found in mPW1PW91, B3LYP, and MP2; however, BH&HLYP suffers from a large RMS error in both the bond length and perpendicular looseness.

For the reactions explored in this paper, the error tables show that B3LYP and mPW1PW91 are not well suited for geometry optimizations for dynamics calculations. Geometries optimized with QCISD are well balanced with respect to perpendicular looseness; however, the method is prohibitively expensive except for small systems. MPW1K predicts saddle point geometries almost as well with only an augmented, polarized valence-double-ζ-basis and a much lower cost, and MPW1K with the larger basis set is more accurate for the full (five-reaction) test set.

TABLE 5: Mean Errors (kcal/mol) for 6-31+G(d,p) Basis

method	MSE[a]	MUE	RMSE	cost
		66 Data		
B3LYP		3.8	4.4	2.4(2)[b]
mPW1PW91		2.8	3.3	2.5(2)
MPW1K		1.6	2.1	2.5(2)
BH&HLYP		3.0	3.9	2.4(2)
MP2		4.6	5.4	2.6(2)
QCISD		3.8	4.4	1.9(4)
		44 Barrier Heights		
B3LYP	−4.1	4.2	4.9	
mPW1PW91	−3.6	3.6	3.8	
MPW1K	−1.1	1.5	1.9	
BH&HLYP	0.5	2.7	3.4	
MP2	5.5	5.8	6.3	
QCISD	3.2	3.5	4.1	
		22 Energies of Reaction		
B3LYP		2.8	3.4	
mPW1PW91		1.3	1.6	
MPW1K		1.7	2.3	
BH&HLYP		3.7	4.7	
MP2		2.1	2.9	
QCISD		3.0	3.5	

[a] Mean *signed* errors for energies of reaction are meaningless since each reaction could be written in either direction. [b] Power of 10 in parentheses.

4.2. Energetics. All calculated values of $V_{\mathrm{f}}^{\ddagger}$, $V_{\mathrm{r}}^{\ddagger}$, and ΔE are given in the Supporting Information. Table 5 compares the mean signed error (MSE), mean unsigned error (MUE), and root-mean-squared error (RMSE) for the barrier heights and reaction energies for the set of 22 reactions optimized using the 6-31+G-

TABLE 6: Mean Errors (kcal/mol) for MG3 Basis

method	MSE	MUE	RMSE	cost
		66 Data		
B3LYP		3.1	3.7	1.6(3)[a]
mPW1PW91		2.7	3.1	1.6(3)
MPW1K		1.4	1.8	1.6(3)
BH&HLYP		2.6	3.3	1.6(3)
MP2		3.7	4.5	3.3(3)
QCISD		2.4	2.8	1.9(5)
		44 Barrier Heights		
B3LYP	−3.5	3.6	4.1	
mPW1PW91	−3.4	3.4	3.6	
MPW1K	−1.0	1.5	1.8	
BH&HLYP	0.6	2.5	3.1	
MP2	3.9	4.3	4.9	
QCISD	2.6	2.7	3.1	
		22 Energies of Reaction		
B3LYP		2.1	2.6	
mPW1PW91		1.3	1.6	
MPW1K		1.4	1.7	
BH&HLYP		2.8	3.7	
MP2		2.5	3.4	
QCISD		1.6	2.0	

[a] Power of 10 in parentheses.

TABLE 7: Mean Errors (kcal/mol) for //MPW1K/6-31+G(d,p) Calculations

single-point energy	MSE	MUE	RMSE	cost
		66 data		
PMP2/6-31+G(d,p)		2.7	3.4	2.5(2)[a]
QCISD/6-31+G(d,p)		3.8	4.4	3.4(2)
QCISD(T)/6-31+G(d,p)		3.1	3.6	3.8(2)
PMP2/MG3		2.1	2.9	3.1(2)
QCISD/MG3		2.3	2.7	1.4(3)
QCISD(T)/MG3		1.2	1.5	1.9(3)
CCSD(T)/MG3		1.2	1.5	2.1(3)
		44 barrier heights		
PMP2/6-31+G(d,p)	3.0	3.3	3.9	
QCISD/6-31+G(d,p)	4.1	4.2	4.8	
QCISD(T)/6-31+G(d,p)	3.0	3.2	3.7	
PMP2/MG3	1.3	2.1	3.0	
QCISD/MG3	2.4	2.6	3.0	
QCISD(T)/MG3	1.0	1.3	1.5	
CCSD(T)/MG3	1.1	1.3	1.6	
		22 energies of reaction		
PMP2/6-31+G(d,p)		1.5	2.0	
QCISD/6-31+G(d,p)		3.0	3.5	
QCISD(T)/6-31+G(d,p)		2.7	3.3	
PMP2/MG3		2.0	2.6	
QCISD/MG3		1.6	2.0	
QCISD(T)/MG3		1.1	1.4	
CCSD(T)/MG3		1.1	1.3	

[a] Power of 10 in parentheses.

(d,p) basis. The first six rows of Table 5 show the MSE, MUE, and RMSE over all 66 data (44 barrier heights, and 22 energies of reaction). Table 6 displays the same errors for the structures optimized using the MG3 basis. Tables 5 and 6 also show the errors averaged separately over the barrier heights and energies of reaction.

Table 7 shows some results for optimizing the saddle point geometry at the MPW1K/6-31+G(d,p) level and then performing single-point energy calculations at that geometry. The table shows that there is little advantage in doing this unless the higher level calculation includes connected triple excitations with a large basis set. But, if the higher-level calculation does include these characteristics, i.e., QCISD(T)/MG3 and CCSD(T)/MG3, then the results are quite accurate. For example, QCISD(T)/MG3//MPW1K/6-31+G(d,p) shows a mean unsigned error in barrier heights of only 1.3 kcal/mol at a cost only 20% larger than MPW1K/MG3 (which has a mean unsigned error in barrier heights of 1.5 kcal/mol) and 100 times faster than the fully optimized QCISD/MG3 calculations (which have a mean unsigned error in barrier heights of 2.7 kcal/mol).

TABLE 8: Root-Mean-Square Errors and Scale Factors for Calculating Zero Point Energies

method	RMS error in ZPE[a]		
	unscaled	scaled	scale factor
MP2/cc-pVDZ	0.33[b]	0.17[b]	0.9790[b]
MPW1K/6-31+G(d,p)	0.70	0.21	0.9515
MPW1K/MG3	0.66	0.24	0.9552

[a] Units are kcal/mol. [b] Ref 37.

The MPW1K method outperforms all other methods tested in accuracy. It is also among the least expensive methods in terms of computational cost. The main source of error in the B3LYP and mPW1PW91 methods comes from a systematic underestimate of the classical barrier height. Similarly, the ab initio methods suffer from a systematic error, but they instead tend to overestimate the barrier height.

5. Summary and Concluding Remarks

This paper expands upon a previous database of classical barrier heights that can be used to test new methods for kinetics calculations and adds a database for saddle point geometries. It uses these databases as test cases and compares the cost and accuracy of a number of methods for calculating saddle point geometries, reaction barrier heights, and reaction energetics. It confirms the success for energies of the MPW1K hybrid density functional method with a small basis, it quantifies the improvement when going to a larger basis, it demonstrates that the method is quite accurate for saddle point geometries as well as energies, and it demonstrates the successful use of the method for calculating saddle point geometries in conjunction with single-point calculations at the QCISD(T) and CCSD(T) levels. For comparison the paper also reports full sets of optimizations with other hybrid density functionals and two ab initio levels with two basis sets, and a total of six single-point strategies are tested. The answer to the question in the title of this paper is “very well indeed, especially considering the low cost.” It is particularly encouraging to note that the hybrid DFT results are much less sensitive to the basis set than are the ab initio ones.

The database is dominated by hydrogen-atom-transfer reactions of neutral species in the gas phase. It will be interesting to test the successful approaches more broadly in the future.

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Supporting Information Available: Tables of gas phase geometries at the sadle point and values of $V_f^{\ddagger}$, $V_r^{\ddagger}$, and ΔE. This material is available free of charge via the Internet at http://pubs.acs.org.

Appendix. Vibrational Frequencies

In a previous paper[37] we developed a database of thirteen anharmonic vibrational zero point energies (ZPEs) for testing and parametrizing vibrational frequencies. Although vibrational frequencies are not used in the present study, we did employ this vibrational ZPE database to develop scale factors for vibrational frequencies calculated both by MPW1K/6-31+G-(d,p) and MPW1K/MG3. The results will be useful for applying

MPW1K methods to chemical reactions, and they are presented in Table 8, where they are compared to the previous[37] results.

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