Development and Assessment of a New Hybrid Density Functional Model for Thermochemical Kinetics

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A new hybrid Hartree−Fock-density functional model called the Becke88−Becke95 1-parameter model for kinetics (BB1K) was optimized against a database of three forward barrier heights, three reverse barrier heights, and three energies of reaction for the reactions in the BH6 representative barrier height database. We then assessed the newly developed BB1K method against a saddle point geometries database, a database of 42 barrier heights, the AE6 representative atomization energy database, a molecular geometries data set, and a set of 13 zero point energies. The results show that BB1K can give excellent saddle point geometries and barrier heights, and its performance for calculating atomization energies is 40% better than MPW1K. Using a mean mean unsigned error criterion that equally weights the errors in barrier heights and in bond energies, the new BB1K method outperforms all other DFT and hybrid DFT methods by a large margin, and we therefore conclude that it is the best density functional-type method for thermochemical kinetics.

1. Introduction

In the past decade, there has been substantial progress in the refinement of functionals for density functional theory (DFT).[1−15] Hybrid Hartree−Fock (HF) density-functional theory (mixing Hartree−Fock theory with pure DFT at the level of the Fock-Kohn−Sham operator, also called hybrid DFT) has been widely used for thermochemistry and has had a remarkable impact on computational chemistry due to its excellent cost-to-performance ratio. Recently we tested[16] many second- and third-generation pure and hybrid DFT methods against the BH6[17] representative barrier height database and the AE6[17] representative atomization energy database (BH6 and AE6 will be further discussed in section 2). Our results show that some pure DFT methods such as VSXC[6] and OLYP[11] can give comparable performance to hybrid DFT methods for atomization energy calculations. However, all tested pure and hybrid DFT methods except MPW1K are less accurate for kinetics (barrier heights) than for thermochemistry (bond energies). MPW1K[18] is the modified Perdew-Wang-1-parameter model for kinetics based on the mPW1PW91[5] model, but with the percentage of Hartree−Fock exchange optimized against a kinetics database including 20 reactions.[18] Several studies[19−35] have demonstrated that the MPW1K model gives remarkably good performance for kinetics.

Our previous evaluations[16,35] showed that the increased percentage of HF exchange in MPW1K deteriorates the atomization energy calculation, although it has only a small effect on the energies of reaction for isogyric reactions. In the present study, we develop a hybrid DFT model that gives better performance than MPW1K on both barrier height and atomization energy calculations. The new method is based on Becke's 1988 gradient corrected exchange functional (Becke88 or B)[36] and Becke's 1995 kinetic-energy-dependent dynamical correlation functional (Becke95 or B95) and is called BB95.[2] Becke also proposed a hybrid version of this model to correct the tendency of density functional exchange to overestimate the nondynamical correlation energy; the resulting one-parameter model is called B1B95. The percentage of HF exchange in the B1B95 method is 28%. (Note that in Gaussian03[37] this is incorrectly coded as 25%). In our previous test,[16] B1B95 gives excellent performance on atomization energy calculations but systematically underestimates the barrier heights. Here we optimize a one-parameter hybrid DFT model especially for thermochemical kinetics based on B exchange and B95 correlation. The resulting model will be called BB1K (Becke88-Becke95 1-parameter model for kinetics).

Section 2 summarizes our kinetics database and test sets and presents the parametrization procedure that was used to obtain the new HDFT model. Section 3 assesses the new method and compares it with other methods. Section 4 presents results and discussion.

2. Databases

2.1. Training Set and Parametrization. To parametrize the new HDFT model, we used a database of 3 forward barrier heights, 3 reverse barrier heights, and 3 energies of reaction for the three reactions in the BH6 database;[17] and this 9-component database is called Kinetics9. We used this small training set because the BH6 representative barrier height database was developed[17] such that the errors calculated for this small database correlate extremely well with errors calculated for a much larger database[23,35] of 44 barrier heights.

The one-parameter hybrid Fock−Kohn−Sham operator can be written as follows:[2,18]

$$F = F^{H} + XF^{HFE} + (1 - X)(F^{SE} + F^{GCE}) + F^{C} \qquad (1)$$

where F^{H} is the Hartree operator (i.e., the nonexchange part of the Hartree−Fock operator), F^{HFE} is the Hartree−Fock exchange operator, X is the fraction of Hartree−Fock exchange, F^{SE} is the Dirac−Slater local density functional for exchange,[38,39] F^{GCE} is the gradient correction for the exchange functional, and F^{C} is the total correlation functional including both local and gradient-corrected parts. In our new HDFT model, we used Becke88 for F^{GCE} and Becke95 for F^{C}. Setting $X = 0.28$ yields

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the B1B95 method of Becke,[2] but instead of using this value, we will use the value that minimizes the root-mean-square error (RMSE) of the nine data in the Kinetics9 database.

The parametrization process was carried out iteratively with the 6-31+G(d,p) basis set.[40,41] We started with QCISD/MG3 geometries for the reactants, products, and transition states and found the optimum X. Then we reoptimized the geometries with this value of X and so forth until the method converged to $X = 0.42$.

The small size of the database greatly accelerated the parametrization procedure as compared to using a larger database. The representative character of the database makes us expect that the parameter obtained from the small database is as good as would be obtained with a much larger database.

2.2. Barrier Height Test Set. The barrier height test set we will use in our assessments consists of the forward and reverse barrier height for 21 of the 22 reactions in Database/3.[35] One of the reactions in Database/3, namely, $H + CH_3OH \rightarrow H_2 + CH_2OH$, is not included in the present test because we are no longer confident that the experimental and theoretical values used for this reaction in the creation of the database are reliable; this reaction is under further investigation in our group. The classical barrier heights used for 20 of the remaining 21 reactions in Database/3 are previously published best estimates of the barrier heights for these reactions, as explained in previous papers.[18,20,23,35] However, we made one change in the database for the present paper. Previously our database had a forward barrier height of 5.7 kcal/mol for $OH + H_2 \rightarrow H_2O + H$. However, Troya et al.[42] obtain a forward barrier of 5.3 kcal/mol. We estimate, on the basis of careful consideration of their paper (in particular the facts that they treated generalized normal modes in rectilinear rather than curvilinear coordinates and that their calculated kinetic isotope effect is too high), that their barrier may still be 0.1−0.2 kcal/mol high, and therefore we are changing the database barrier to 5.1 kcal/mol for the forward reaction and 21.2 kcal/mol for the reverse barrier height. With the improvement of the best estimate of the barrier height of the reaction $OH + H_2 \rightarrow H_2O + H$, the updated 42 barrier heights for the 21 reactions will be called the BH42/03 database, and they are given in the Supporting Information.

2.3. Bond Energy Test Set. We also tested the new HDFT method against the AE6[17] representative atomization energy database. The AE6 set of atomization energies consists of SiH_4, S_2, SiO, C_3H_4 (propyne), $C_2H_2O_2$ (glyoxal), and C_4H_8 (cyclobutane). This set of atomization energies is very diverse, if one considers its size, and it was developed such that performance on this database is indicative of performance on a much larger 109-molecule database.[35,43] In this paper all errors for the AE6 database are divided by the average number of bonds (4.83) in the molecules of this database; this yields a mean error on a per bond basis, so these comparisons provide a test of the accuracy of calculated bond energies.

2.4. Saddle Point Geometries. The database of saddle point geometries comes from the previous work.[20,23] The test set consists of five reactions where very high-level calculations of saddle point geometries are available.[44−47] These data for saddle point geometries are listed in Table 1. These 15 data are called the SPG15/01 database. The perpendicular looseness has been defined[20,23] as the sum of the forming and breaking bond distances; this is a measure of the looseness of the saddle point structure in the direction perpendicular to the reaction coordinate.

2.5. Vibrational Zero Point Energies Database. A database of thirteen anharmonic vibrational zero point energies (ZPEs) has been presented in a previous paper,[48] on the basis of the work of Martin.[49] This is called the ZPE13/99 database. We will employ this vibrational ZPE database to develop scale factors for vibrational frequencies calculated both by BB1K/6-31+G(d,p) and by BB1K/MG3S. The scale factors are optimized to minimize the root-mean-square errors in the calculated ZPEs for these 13 molecules. In principle, such scale factors account for both anharmonicity and the errors in the calculated harmonic frequencies; in practice, the latter is much more important than the former.

TABLE 1: Best Estimates of Saddle Point Geometries for A + BC → AB + C[a]

reaction A + BC	$R^{\neq}_{AB}$	$R^{\neq}_{BC}$	$R^{\neq}_{sum}$	$\theta^{\neq}_{ABC}$	ref
H + HCl → H_2 + Cl	0.981	1.431	2.412	180	44
H + H_2 → H_2 + H	0.930	0.930	1.860	180	45
H + ClH′ → HCl + H′	1.480	1.480	2.960	180	44
H + HO → H_2 + O	0.894	1.215	2.109	180	47
F + H_2 → HF + H	1.546	0.771	2.317	119	46

[a] Bond distances are in angstroms, and bond angles, degrees.

2.6. Geometries, Basis Sets, and Spin−Orbit Energy. Whereas the tests in sections 2.1, 2.4, and 2.5 involve geometry optimization with each level of theory tested, all calculations in sections 2.2 and 2.3 are single-point calculations at QCISD/MG3 geometries, where QCISD is the quadratic configuration interaction with single and double excitations,[50] and MG3 is the modified[51,52] G3Large[53] basis set. The MG3 basis set,[51] also called G3LargeMP2,[52] is the same as 6-311++G(3d2f,2df,2p)[54] for H−Si, but improved[53] for P−Ar. The QCISD/MG3 geometries for molecules and saddle points in the AE6 database and the BH42/03 database of 42 barrier heights can be obtained from the Truhlar group database website.[55] We tested the new method with two highly recommended basis sets, namely a recommended[20,43] augmented polarized valence double-ζ set, 6-31+G(d,p),[40,41] and a recommended augmented polarized triple-ζ set, MG3S. In the tables, 6-31+G(d,p) is abbreviated DIDZ (desert-island double-ζ). The MG3S basis[43] is the same as MG3 except it omits diffuse functions on hydrogens.

To test the performance for calculating equilibrium geometries, we compare the BB1K method to four other methods using a set of 23 molecules that consists of the 13 molecules in the ZPE database and the 10 molecules in the AE6 and BH6 databases. We include all unique bond angles and bond distances in this 23 molecule set, giving a total of 34 bond lengths and 11 bond angles, for a total of 45 data. This geometry data set is called G45/04. The experimental data for bond lengths and angles are taken from Computational Chemistry Comparison and Benchmark DataBase[56] (CCCBDB), and they are listed in the Supporting Information.

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.[51] All calculations were performed with the Gaussian03 program.

3. Assessment of Methods

We tested our new HDFT model, which is called BB1K, against the saddle point geometries test set, the BH42/03 database of 42 barrier heights, the BH6 representative barrier height database, the AE6 representative atomization energy database, and the G45/04 geometry data set.

For the saddle point geometries, we compared BB1K results to some previously published results for other methods including B3LYP,[36,57,58] BH&HLYP,[59] mPW1PW91,[5] Møller−Plesset second-order perturbation theory (MP2),[60] and QCISD and also to new results obtained here for the B97-2 hybrid DFT method.

TABLE 2: Mean Errors (Å) in Internuclear Distances at the Saddle Point of the Five Reactions in Table 1

	bond distance			perpendicular losseness			
method	MSE	MUE	RMSE	MSE	MUE	RMSE	ref
BB1K/DIDZ	0.00	0.03	0.04	0.01	0.01	0.02	this work
BB1K/MG3S	0.00	0.02	0.02	0.00	0.01	0.01	this work
B1B95/DIDZ[a]	0.01	0.04	0.06	0.03	0.03	0.05	this work
B1B95/MG3S[a]	0.01	0.03	0.04	0.01	0.02	0.03	this work
BB95/DIDZ [a]	0.05	0.07	0.13	0.09	0.09	0.14	this work
BB95/MG3S [a]	0.04	0.06	0.11	0.07	0.07	0.11	this work
B97-2/DIDZ[a]	0.02	0.06	0.09	0.04	0.04	0.07	this work
B97-2/MG3S[a]	0.01	0.05	0.07	0.02	0.03	0.05	this work
MPW1K/DIDZ	0.00	0.02	0.03	−0.01	0.02	0.02	20
MPW1K/MG3S	−0.01	0.01	0.02	−0.02	0.02	0.02	this work
B3LYP/DIDZ[a]	0.03	0.07	0.12	0.07	0.07	0.11	20
B3LYP/MG3[a]	0.01	0.05	0.09	0.03	0.06	0.09	20
BH&HLYP/DIDZ	−0.01	0.04	0.06	−0.01	0.04	0.06	20
BH&HLYP/MG3	−0.01	0.03	0.05	−0.02	0.04	0.05	20
mPW1PW91/DIDZ[a]	0.01	0.03	0.06	0.03	0.03	0.04	20
mPW1PW91/MG3[a]	0.01	0.04	0.08	0.02	0.03	0.05	20
MP2/DIDZ	−0.03	0.03	0.05	−0.05	0.05	0.07	20
MP2/MG3	−0.03	0.04	0.06	−0.07	0.07	0.08	20
QCISD/DIDZ	−0.01	0.03	0.04	−0.02	0.03	0.04	20
QCISD/MG3	−0.01	0.02	0.03	−0.01	0.02	0.03	20

[a] The results for B97-2, B1B95, BB95, B3LYP, and mPW1PW91 are calculated only for the first four reactions in Table 1, because they do not yield a finite-distance saddle point for $F + H_2 \rightarrow HF + H$.

B97-2 is Wilson, Bradley, and Tozer's[13] modification to Becke's 1997 functional (B97).[4] We tested B97-2 because B1B95 and B97-2 were the two best methods of our previous study as judged by the mean mean unsigned error (MMUE) criterion defined in our previous paper:[16]

$$\text{MMUE} = {}^1/_4[\text{MUE(BH6,DIDZ)} + \text{MUE(BH6,MG3S)} + \text{MUE(AE6,DIDZ)} + \text{MUE(AE6,MG3S)}] \quad (2)$$

where MUE denotes mean unsigned error (also called mean absolute error). The motivation for this criterion, as presented previously, is that it is desirable for a hybrid DFT method to give good results for both bond energies and barrier heights with both polarized double-ζ and polarized triple-ζ basis sets. (The smaller basis sets are important because one of the attractive features of hybrid DFT is its applicability to large systems, for which larger basis sets can be cost prohibitive.) Note that the MUE quantities for the AE6 database in eq 2 are on a per bond basis.

For the 42 barrier heights in the BH42/03 database, we compared BB1K and B97-2 results to previously published results obtained with the MPW1K, B3LYP, mPW1PW91, and QCISD methods.

For the AE6 and BH6 representative benchmark database, we compared BB1K to our recent test results[16] for B97-2, MPW1K, B1B95, B98, B97-1, and B3LYP (listed in order of increasing MMUE). B98 is Schmider and Becke's 1998 revision[61] of the B97 functional.[4] B97-1 is Hamprecht, Cohen, Tozer, and Handy's modification[7] of the B97 functional.[4]

For the equilibrium geometry optimizations, we compared BB1K to B3LYP, B1B95, MPW1K, and QCISD.

4. Results and Discussion

4.1. Saddle Point Geometries. Table 2 summarizes the error in $R^{\neq}_{\text{forming bond}}$ and $R^{\neq}_{\text{breaking bond}}$ and in the perpendicular looseness for the five reactions (four for B97-2, B1B95, BB95, B3LYP, and mPW1PW91) in Table 1. The fifth reaction $F + H_2 \rightarrow HF + H$ was left out for B97-2, B1B95, BB95, B3LYP and mPW1PW91 because these methods predict that there is a monotonically downhill reaction path for this reaction; thus they predict that the highest-energy point on the reaction path is at reactants where the making bond length is ∞. Table 2 shows that BB1K and MPW1K give the lowest mean unsigned error, mean signed error (MSE), and root-mean-squared error in bond length and perpendicular looseness for both the DIDZ and MG3S basis sets. When comparing BB1K to MPW1K, we see that MPW1K performs slightly better for bond length calculations, whereas BB1K is slightly better for the perpendicular looseness. Table 2 also shows that the B97-2, B1B95, BB95, B3LYP, and mPW1PW91 methods have high RMS errors, and they predict looser saddle points in the perpendicular direction; they tend to overestimate the sum of the bond lengths of the making bonds and breaking bonds at the saddle point. MP2 tends to predict tight saddle points, as indicated by the observation that it gives the most negative MSE for perpendicular looseness. The performance of QCISD is slightly worse than BB1K and MPW1K, although it is the most expensive method in the table. BH&HLYP does not have a systematic error in perpendicular looseness, but it suffers from a large RMS error in bond length and perpendicular looseness.

TABLE 3: Mean Errors (kcal/mol) for the 42 Barrier Heights in the BH42/03 Database[a]

method	MSE	MUE	RMSE	ref
BB1K/DIDZ	−0.8	1.4	1.9	this work
BB1K/MG3S	−0.6	1.2	1.5	this work
B1B95/DIDZ	−3.1	3.1	3.5	this work
B1B95/MG3S	−2.8	2.8	3.1	this work
BB95/DIDZ	−8.6	8.6	9.3	this work
BB95/MG3S	−8.2	8.2	9.0	this work
B97−2/DIDZ	−3.0	3.3	3.9	this work
B97−2/MG3S	−2.8	3.1	3.6	this work
MPW1K/DIDZ	−0.8	1.5	2.0	17 updated[b]
MPW1K/MG3S	−0.7	1.4	1.8	17 updated
B3LYP/DIDZ	−4.6	4.7	5.4	17 updated
B3LYP/MG3S	−4.4	4.3	4.9	17 updated
mPW1PW91/DIDZ	−3.8	3.8	4.0	17 updated
mPW1PW91/MG3S	−3.5	3.6	3.8	17 updated
QCISD/DIDZ	4.1	4.2	4.7	17 updated
QCISD/MG3	2.7	2.8	3.2	17 updated

[a] Geometies used are QCISD/MG3. [b] The results for B3LYP, MPW1K, mPW1PW91, and QCISD are recalculated from the original data of ref 17, where they were compared to the Database/3 barrier heights.

4.2. Barrier Heights. All calculated values of the forward and reverse barrier heights of the reactions in the BH42/03 database are given in the Supporting Information. Table 3 compares the MSE, MUE, and RMSE for the 42 barrier heights for the set of 21 reactions. Table 3 shows that BB1K gives the lowest MUE and RMSE for both the DIDZ and MG3S basis sets. The second best method is MPW1K. The performance of B97-2 and B1B95 is slightly better than mPW1PW91, but they still systematically underestimate the barrier heights. BB95 (a pure DFT method) and B3LYP (the most popular hybrid DFT method) are the least accurate methods (of those tested) for calculating barrier heights.

4.3. Vibrational Frequencies Scale Factor. Calculation of vibrational frequencies is very important for theoretical kinetics. It is well-known that the HF method tends to overestimate the vibrational frequencies, and Table 4 confirms this by showing that HF vibrational frequencies need to be scaled by about 0.92 to reproduce accurate zero point energies. We incorporated 42% of HF exchange in our BB1K model, so the vibrational frequency calculations are deteriorated as compared to B1B95. We employed the ZPE13/99 database[48,49] of thirteen anharmonic vibrational zero point energies to determine the vibrational

TABLE 4: Root-Mean-Square Error (kcal/mol) and Scale Factor for Calculating Zero Point Energies

	RMS error in ZPE			
method	unscaled	scaled	scale factor	ref
BB1K/DIDZ	0.62	0.15	0.9561	this work
BB1K/MG3S	0.59	0.18	0.9590	this work
B1B95/DIDZ	0.37	0.11	0.9735	this work
B1B95/MG3S	0.35	0.14	0.9758	this work
BB95/DIDZ	0.21	0.11	1.0139	this work
BB95/MG3S	0.21	0.11	1.0144	this work
MPW1K/DIDZ	0.70	0.21	0.9515	20
MPW1K/MG3S	0.60	0.18	0.9581	this work
B3LYP/DIDZ	0.23	0.09	0.9843	this work
B3LYP/MG3S	0.23	0.11	0.9851	this work
HF/DIDZ	1.21	0.25	0.9173	this work
HF/MG3S	1.16	0.27	0.9210	this work

TABLE 5: Mean Errors (kcal/mol for Barriers and kcal/mol per Bond for Atomization Energies) for BH6 and AE6 Benchmarks with QCISD/MG3 Geometries

		BH6		AE6			
method	X^a	MSE	MUE	MSE	MUE	MMUE[b]	ref[c]
BB1K/DIDZ	0.42	−1.0	1.4	−1.8	1.8	1.4	this work
BB1K/MG3S	0.42	−1.0	1.1	−1.1	1.3		
B1B95/DIDZ	0.28	−3.2	3.2	−0.8	0.9	2.0	16
B1B95/MG3S	0.28	−3.1	3.1	−0.2	0.6		
B97−2/DIDZ	0.21	−2.9	3.1	−0.8	0.8	2.0	16
B97−2/MG3S	0.21	−2.9	3.2	−0.1	0.7		
MPW1K/DIDZ	0.428	−1.0	1.4	−3.1	3.1	2.1	16
MPW1K/MG3S	0.428	−1.1	1.4	−2.3	2.3		
B98/DIDZ	0.2198	−4.1	4.1	−1.3	1.3	2.5	16
B98/MG3S	0.2198	−4.0	4.0	−0.4	0.6		
B97−1/DIDZ	0.21	−4.2	4.2	−1.2	1.2	2.6	16
B97−1/MG3S	0.21	−4.1	4.1	−0.4	0.9		
B3LYP/DIDZ	0.20	−5.0	5.0	−1.4	1.5	3.1	16
B3LYP/MGS3S	0.20	−5.0	4.7	−0.6	0.7		
BB95/DIDZ	0.00	−8.3	8.3	1.4	1.7	5.1	16
BB95/MG3S	0.00	−8.0	8.0	2.0	2.4		
HF/DIDZ		12.4	12.4	−30.9	30.9	21.4	17
HF/MG3S		12.3	12.3	−30.1	30.1		

[a] X denotes the fraction of the HF exchange in the DFT methods. [b] MMUE is defined in eq 2 and is a measure of quality of a method, not only for the DIDZ basis. [c] This is the reference for the determining MMUE; references for methods are given in the text.

frequency scale factor for BB1K/6-31+G(d,p) and BB1K/MG3S. They are listed with scale factors for MPW1K and some other methods in Table 4. The key conclusion to be drawn from Table 5 is that the scale factor for the new method is not too far from unity. Furthermore, if we divide the RMS errors by the average number of bonds (2.00) per molecule in the zero point energy database, we see that the errors after scaling are only 0.08−0.09 kcal/mol per bond, which is smaller than the error in the electronic structure part.

The scale factors will be useful for applying BB1K methods to chemical reaction kinetics calculations.

4.4. AE6 and BH6 Benchmarks. Table 5 summarizes the mean errors for the benchmark BH6 and AE6 representative databases for the BB1K method and some other hybrid DFT methods as well as the BB95 pure DFT method and also the pure Hartree−Fock method. Note that the MSEs and MUEs for AE6 are given on a per bond basis as described in our previous paper[16] and in sections 2.2 and 3. If we use the MMUE criterion defined in eq 2 to measure the quality of the methods listed in Table 5, we can see that BB1K outperforms all other methods. Even though the MUE(AE6) of BB1K is higher than B97-2, B1B95, B98, B97-1, and B3LYP, it gives better performance for atomization energy calculations than MPW1K.

TABLE 6: Mean Errors (kcal/mol for Barriers and kcal/mol per Bond for Atomization Energies) for BH6 and AE6 Benchmarks with Consistently Optimized Geometries

		BH6		AE6		
method	X	MSE	MUE	MSE	MUE	MMUE
BB1K/DIDZ	0.42	−1.0	1.4	−1.8	1.8	1.4
BB1K/MG3S	0.42	−1.0	1.1	−1.1	1.2	
B1B95/DIDZ	0.28	−3.1	3.1	−0.8	0.9	1.9
B1B95/MG3S	0.28	−3.0	3.0	−0.1	0.6	
B97−2/DIDZ	0.21	−2.5	3.3	−0.8	0.8	2.0
B97−2/MG3S	0.21	−2.6	3.1	−0.1	0.7	
MPW1K/DIDZ	0.428	−1.0	1.4	−3.1	3.1	2.0
MPW1K/MG3S	0.428	−1.1	1.4	−2.2	2.2	
B3LYP/DIDZ	0.20	−4.6	5.0	−1.4	1.5	2.9
B3LYP/MGS3S	0.20	−4.4	4.4	−0.6	0.6	
HF/DIDZ		13.5	13.5	−30.9	30.9	21.9
HF/MG3S		13.4	13.4	−29.9	29.9	

TABLE 7: Mean Errors of Bond Lengths (Å) and Bond Angles (deg) for 23 Molecules

		bond length		bond angle	
method	X	MSE	MUE	MSE	MUE
BB1K/MG3S	0.42	−0.013	0.014	−0.61	0.72
B1B95/MG3S	0.28	−0.007	0.008	−0.22	0.88
MPW1K/MG3S	0.428	−0.013	0.014	−0.61	0.72
B3LYP/MGS3S	0.20	−0.003	0.006	−0.52	0.68
QCISD/MG3		−0.003	0.005	−0.45	0.65

If we compare the MSE and MUE of BB1K, B1B95, BB95, and B97-2 using the BH6 benchmark in Table 5 to the MSE and MUE for the entire 42 barrier heights of BH42/03 database in Table 3, we see that the errors (especially MUE) for BH6 correlate fairly well with the errors using the much larger database. This again confirms the representative characteristics of the BH6 database developed on the basis of 80 electronic structure methods.[17]

We also tested BB1K with consistently optimized geometries (that is, geometries optimized by BB1K itself rather than the more expensive QCISD method), and the results are listed with the results for four other methods in Table 6. If we compare Table 6 to Table 5, we see that they give almost identical results except some slight improvements for B1B95 and MPW1K. This confirms our past experience[16,17,35,43] that the QCISD/MG3 geometries are well suited for testing and developing methods.

4.5. Molecular Geometries. Table 7 summarizes the mean errors in bond lengths and bond angles calculated by BB1K and four other methods. It is well-known that HF tends to underestimate bond lengths. Because we incorporate 42% HF exchange in the BB1K model, the bond lengths calculated by BB1K are slightly deteriorated as compared to B3LYP and B1B95; these two HDFT functionals only have 20% and 28% HF exchange, respectively. This is consistent with the results in the previous section, where we showed that the excess amount of HF exchange in BB1K also deteriorated the atomization energies calculation. However, if we consider the performances for calculating the saddle point geometries and for calculating equilibrium geometries together (just as we use MMUE criterion for judging the performance for energetics calculations) we can draw the same conclusion that the BB1K is the best HDFT method for thermochemical kinetics.

From Tables 2 and 7, we see that QCISD/MG3 method gives good performance for the calculations of saddle point geometries and equilibrium geometries, and this is why the QCISD/MG3 geometries are well suited for testing and developing methods.

5. Concluding Remarks

This paper developed a new hybrid DFT method for thermochemical kinetics from a small but representative training set. The resulting method, BB1K, was assessed against the SPG15/02 saddle point geometries database, against the BH42/03 database of 42 barrier heights, against the AE6 representative atomization energy database, against the BH6 representative barrier height database, against the ZPE13/99 zero point energy database, and against the G45/04 geometry data set of bond distances and bond angles. BB1K was also compared to some standard methods. The assessment and comparison demonstrate that BB1K is quite accurate for calculating saddle point geometries and barrier heights. The performance of BB1K for calculating atomization energies is better than another hybrid DFT model that has been found to be very useful for kinetics, MPW1K.

The search for accurate and efficient methods for computational kinetics is an ongoing effort. The present contribution shows that considerable progress is still possible. The mean mean unsigned error criterion of this paper (column MMUE in Table 5) and ref 16 is an attempt to provide a measure of the usefulness of computational methods for thermochemical kinetics by employing an equal weighting of error in barrier heights and bond energies, and it indicates that the new BB1K method provides a considerable improvement for thermochemical kinetics over all other hybrid DFT methods that are available at the present time.

The keywords required to carry out BB1K/DIDZ calculations with the Gaussian03 program are bb95/6-31+G(d,p) and IOp(3/76 = 0580004200). See also http://comp.chem.umn.edu/info/bb1k.htm.

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Supporting Information Available: The calculated barrier heights and best estimate for the BH42/03 database and the optimized saddle point geometries are given in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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