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Benchmark Database of Barrier Heights for Heavy Atom Transfer, Nucleophilic Substitution, Association, and Unimolecular Reactions and Its Use to Test Theoretical Methods

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A benchmark database of forward and reverse barrier heights for 19 non-hydrogen-transfer reactions has been developed by using Weizmann 1 calculations, and 29 DFT methods and 6 ab initio wave-function theory (WFT) methods have been tested against the new database as well as against an older database for hydrogen atom transfer reactions. Among the tested hybrid DFT methods without kinetic energy density, MPW1K is the most accurate model for calculations of barrier heights. Among the tested hybrid meta DFT methods, BB1K and MPWB1K are the two most accurate models for the calculations of barrier heights. Overall, the results show that BB1K and MPWB1K are the two best DFT methods for calculating barrier heights, followed in order by MPW1K, MPWKCIS1K, B1B95, MPW1B95, BHandHLYP, B97-2, mPW1PW91, and B98. The popular B3LYP method has a mean unsigned error four times larger than that of BB1K. Of the methods tested, QCISD(T) is the best ab initio WFT method for barrier height calculations, and QCISD is second best, but QCISD is outperformed by the BB1K, MPWB1K, MPWKCIS1K, and MPW1K methods.

1. Introduction

Density-functional theory (DFT) methods[1−59] have been shown to be more efficient than wave-function theory (WFT) methods for computational thermochemistry and thermochemical kinetics due to their excellent cost-to-performance ratio. However pure DFT methods overestimate bond energies and underestimate barrier heights (BHs) for chemical reactions. One of the practical ways to tackle this problem is to use hybrid DFT[11] (mixing Hartree−Fock (HF) theory with Kohn−Sham DFT at the level of the Fock−Kohn−Sham operator). Hybrid DFT methods can be justified theoretically by the adiabatic connection theorem (ACT).[56] Nevertheless the most popular hybrid DFT method, B3LYP,[6,11,12] is only parametrized against a data set for thermochemistry, and it significantly underestimates BHs. The first successful hybrid DFT model for thermochemical kinetics was MPW1K.[30] It was parametrized against a database of 44 BHs of 22 reactions, 21 of which are hydrogen-transfer (HT) reactions. This database of BHs was updated later as BH44/3 (one part of Database/3),[42,57] BH42/04,[50,53,58] and HTBH38/04[59] by taking into account some new experimental and theoretical results in the literature and by leaving out data that are not reliable or that are not for HT reactions. This database was successfully employed in conjunction with other databases to parametrize or test some new methods such as multi-coefficient correlation methods (MCCM/3),[57] hybrid meta DFT methods (BB1K,[50] MPWB1K,[53] and TPSS1KCIS,[59] where "meta" means that the hybrid density functional also depends on the Kohn−Sham orbitals in the form of a kinetic energy density), and multi-coefficient extrapolated DFT methods (MC3BB,[58] MC3MPW,[58] and a suite of methods in a previous paper[59]). Since this database mainly consists of BHs for HT reactions, and in its current form, HTBH38/04, it contains *only* HT BHs, one of the goals of the present paper is to develop a database of BHs for non-HT reactions, and we will employ this new database to assess some hybrid and hybrid meta DFT methods.

A brief comment on notation is useful here. Both "Kohn-Sham DFT" and "hybrid DFT" are legitimate forms of DFT because the "Hartree-Fock exchange" (also called "exact exchange") included in hybrid DFT is computed from orbitals that are functionals of the density. The "pure" (or "Kohn−Sham") density functionals depend both directly on the density (first rung of "Jacob's ladder"[46]) and on the gradient magnitude (so-called generalized gradient approximation or GGA). The meta functionals depend on kinetic energy density, which is computed from orbitals that are functionals of the density, so meta DFT is also a legitimate form of DFT. The present article does not consider density functionals with more complicated dependencies on the density or orbitals. Thus the methods considered here differ in the choice of GGA, in the way that kinetic energy density is or is not included, and in the fraction of Hartree−Fock exchange. We sometimes distinguish pure DFT, meta DFT, hybrid DFT, and hybrid Meta DFT, but we could equally well just call each of these DFT.

Section 2 explains the theories, databases, and functionals used in the present work. Section 3 presents results and discussion, and section 4 has concluding remarks.

2. Theory and Databases

2.1. Weizmann-1 (W1) Theory. Whereas the HTBH database is primarily built on theoretically corrected experimental data, we used a different approach in the present study. In particular, to obtain the best estimates for the BHs in the new database, we employed the W1 method for most reactions. This method was developed by Martin and Oliveira, and it is a method designed to extrapolate to the complete basis limit of a CCSD(T)[60] calculation. Note that W1 results are not "exact",

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TABLE 1: Components of W1 Calculations for BHs (kcal/mol)

reaction	barrier[a]	SCF limit	CCSD limit	(T) limit	core correlation and relativistic	S−O coupling	final BH
$H\cdot + N_2O \rightarrow OH\cdot + N_2$	$V_f^{\neq}$	27.79	−9.25	−0.50	0.10	0.00	18.14
	$V_r^{\neq}$	124.05	−32.64	−7.96	−0.03	−0.20	83.22
$H + FH \rightarrow HF + H$	$V_f^{\neq}$	57.72	−14.02	−1.48	−0.05	0.00	42.18
	$V_r^{\neq}$	57.72	−14.02	−1.48	−0.05	0.00	42.18
$H + FCH_3 \rightarrow HF + CH_3$	$V_f^{\neq}$	47.16	−14.72	−2.07	0.01	0.00	30.38
	$V_r^{\neq}$	73.66	−13.36	−3.34	0.07	0.00	57.02
$H + F_2 \rightarrow HF + F$	$V_f^{\neq}$	−9.54	12.18	−0.41	0.04	0.00	2.27
	$V_r^{\neq}$	123.35	−12.04	−5.56	0.05	0.38	106.18
$CH_3 + FCl \rightarrow CH_3F + Cl$	$V_f^{\neq}$	16.74	−6.65	−2.71	0.05	0.00	7.43
	$V_r^{\neq}$	78.49	−13.79	−4.54	0.00	0.84	60.17
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	$V_f^{\neq}$	7.70	−7.64	−2.84	0.01	0.00	−2.78
	$V_r^{\neq}$	28.64	−8.14	−3.17	0.24	0.00	17.33
$OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$ [b]	$V_f^{\neq}$	19.07	−5.66	−2.46	0.15	0.00	10.96
	$V_r^{\neq}$	53.70	−4.06	−2.43	0.26	0.00	47.20
$H + N_2 \rightarrow HN_2$	$V_f^{\neq}$	22.91	−7.77	−0.55	0.10	0.00	14.69
	$V_r^{\neq}$	13.55	−1.88	−0.92	−0.03	0.00	10.72
$H + CO \rightarrow HCO$	$V_f^{\neq}$	9.05	−5.35	−0.54	0.02	0.00	3.17
	$V_r^{\neq}$	17.31	5.65	−0.40	0.13	0.00	22.68
$H + C_2H_4 \rightarrow CH_3CH_2$	$V_f^{\neq}$	9.67	−7.13	−0.55	0.05	0.00	2.05
	$V_r^{\neq}$	46.79	−2.22	−2.45	−0.04	0.00	42.08
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	$V_f^{\neq}$	23.54	−14.94	−2.07	0.32	0.00	6.85
	$V_r^{\neq}$	41.36	−6.36	−2.14	0.11	0.00	32.97
$HCN \rightarrow HNC$	$V_f^{\neq}$	47.38	0.86	−0.41	0.33	0.00	48.16
	$V_r^{\neq}$	37.65	−3.82	−0.80	0.08	0.00	33.11

[a] $V_f^{\neq}$ denotes forward BH, and $V_r^{\neq}$ denotes reverse BH. [b] This denotes the reaction between the reactant complex and product complex for the previous S_N2 reaction.

but all experience in the literature is consistent with the fact that the complete basis set limit of CCSD(T) should be accurate to better than 1 kcal/mol for the BHs of most reactions. Thus W1 theory should be good enough for testing any methods whose errors exceed this. Recently Coote[61] used the W1 model to obtain reference data for some hydrogen abstraction reactions. Boese and Martin[55] also used W1 and W2 theory to calculate best estimates for some reactions. The strength and limitations of W1 theory have been described elsewhere.[62−66] It is hard to imagine any other way to get results of benchmark accuracy for most of the reactions studied here; extracting the BH from experiment is usually not sufficient for the required accuracy because of uncertainties in the experimental results and because of the difficulty of inverting the experimental data to obtain a classical BH, which cannot be directly observed.

2.2. Benchmark Database of BHs for Non-HT Reactions. The new database consists of forward and reverse BHs for 19 reactions, which consist of 6 heavy-atom transfer reactions, 4 bimolecular nucleophilic substitution (S_N2) reactions, 4 unimolecular nucleophilic substitution reactions for reactions of the reactant complex and product complex for the 4 S_N2 reactions, and 5 association or non-nucleophilic-substitution unimolecular reactions. The best estimates of the BHs of three of the four S_N2 reactions are taken from Parthiban et al.;[63] two of these are based on W2[62] calculations, and we obtain 3.10 kcal/mol for the forward and reverse BHs for the reaction $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$ by a semiempirical adjustment to experiment.[67] The fourth reaction, $OH^- + CH_3F$, is based on W1 calculations performed in the present study. The best estimates for the forward and reverse BHs of one of the heavy-atom transfer reactions, namely, $H + ClH \rightarrow HCl + H$, are taken from the BH42/04 database.[50,53,58] The forward BH of the reaction $H + C_2H_4$ is taken from a dynamics study,[68] and the reverse reaction BH is calculated by using the energy of reaction obtained by W1 and the forward BH. The best estimates for the rest of the reactions are obtained by W1 calculations. The results of the W1 calculations are summarized in Table 1, and the new database is described in Table 2.

2.3. HTBH38/04 Database. The HTBH38/04 database is taken from a previous paper.[59] It consists of 38 transition-state

TABLE 2: Benchmark Database of BHs for Non-HT Reactions[a]

reactions	barrier[a]	best estimate (kcal/mol)	ref
Heavy-Atom Transfer Reactions			
$H + N_2O \rightarrow OH + N_2$	$V_f^{\neq}$	18.14	this work
	$V_r^{\neq}$	83.22	this work
$H + FH \rightarrow HF + H$	$V_f^{\neq}$	42.18	this work
	$V_r^{\neq}$	42.18	this work
$H + ClH \rightarrow HCl + H$	$V_f^{\neq}$	18.00	30,34
	$V_r^{\neq}$	18.00	30,34
$H + FCH_3 \rightarrow HF + CH_3$	$V_f^{\neq}$	30.38	this work
	$V_r^{\neq}$	57.02	this work
$H + F_2 \rightarrow HF + F$	$V_f^{\neq}$	2.27	this work
	$V_r^{\neq}$	106.18	this work
$CH_3 + FCl \rightarrow CH_3\ F + Cl$	$V_f^{\neq}$	7.43	this work
	$V_r^{\neq}$	60.17	this work
Nucleophilic Substitution Reactions			
$F^- + CH_3F \rightarrow FCH_3 + F^-$	$V_f^{\neq}$	−0.34	63
	$V_r^{\neq}$	−0.34	63
$F^-\cdots CH_3F \rightarrow FCH_3 \cdots F^-$	$V_f^{\neq}$	13.38	63
	$V_r^{\neq}$	13.38	63
$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	$V_f^{\neq}$	3.10	67
	$V_r^{\neq}$	3.10	67
$Cl^-\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$	$V_f^{\neq}$	13.61	63
	$V_r^{\neq}$	13.61	63
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	$V_f^{\neq}$	−12.54	63
	$V_r^{\neq}$	20.11	63
$F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$	$V_f^{\neq}$	2.89	63
	$V_r^{\neq}$	29.62	63
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	$V_f^{\neq}$	−2.78	this work
	$V_r^{\neq}$	17.33	this work
$OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$	$V_f^{\neq}$	10.96	this work
	$V_r^{\neq}$	47.20	this work
Unimolecular and Association Reactions			
$H + N_2 \rightarrow HN_2$	$V_f^{\neq}$	14.69	this work
	$V_r^{\neq}$	10.72	this work
$H + CO \rightarrow HCO$	$V_f^{\neq}$	3.17	this work
	$V_r^{\neq}$	22.68	this work
$H + C_2H_4 \rightarrow CH_3CH_2$	$V_f^{\neq}$	1.72	68
	$V_r^{\neq}$	41.75	68, this work
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	$V_f^{\neq}$	6.85	this work
	$V_r^{\neq}$	32.97	this work
$HCN \rightarrow HNC$	$V_f^{\neq}$	48.16	this work
	$V_r^{\neq}$	33.11	this work

[a] $V_f^{\neq}$ denotes forward BH, and $V_r^{\neq}$ denotes reverse BH.

TABLE 3: Summary of the DFT Methods Tested

method	X[a]	year	type	exchange[b]/correlation[c] functional	refs
LSDA	0	1981	pure	Slater's local Perdew−Wang local	9, 70
BP86	0	1988	pure	Becke88 Perdew's 1986 GGA	4, 5
BLYP	0	1988	pure	Becke88 Lee−Yang−Parr	5, 6
BHandHLYP	50	1993	HDFT	Becke88 Lee−Yang−Parr	5, 6, 10
B3LYP	20	1994	HDFT	Becke88 Lee−Yang−Parr	5, 6, 12
BB95	0	1996	MDFT	Becke88 Becke95	5, 13
B1B95	25	1996	HMDFT	Becke88 Becke95	5, 13
PBE	0	1996	pure	PBE PBE	14
PBE1PBE	25	1996	HDFT	PBE PBE	14
mPWPW91	0	1998	pure	modified Perdew−Wang Perdew−Wang91	8, 19
mPW1PW91	25	1998	HDFT	modified Perdew−Wang Perdew−Wang91	8, 19
mPWLYP	0	1998	pure	modified Perdew−Wang Lee−Yang−Parr	6, 19
VSXC	0	1998	MDFT	VSXC VSXC	21
B97-1	21	1998	HDFT	B97-1 B97-1	22
B98	21.98	1998	HDFT	B98 B98	20
MPW1K	42.8	2000	HDFT	modified Perdew−Wang Perdew−Wang91	19, 24
B97-2	21	2001	HDFT	B97-2 B97-2	22
O3LYP	11.61	2001	HDFT	OPTX Lee−Yang−Parr	32, 33
TPSS	0	2003	MDFT	TPSS TPSS	46, 48
TPSSh	10	2003	HMDFT	TPSS TPSS	46, 48
TPSSKCIS	0	2004	MDFT	TPSS KCIS	24, 25, 40, 46, 48
mPWKCIS	0	2004	MDFT	modified Perdew−Wang KCIS	13, 24, 25, 40
X3LYP	21.8	2004	HDFT	Becke88 + PW91 Lee−Yang−Parr	5, 6, 8, 49
BB1K	42	2004	HMDFT	Becke88 Becke95	5, 13, 50
MPW1B95	31	2004	HMDFT	modified Perdew−Wang Becke95	13, 19, 53
MPWB1K	44	2004	HMDFT	modified Perdew−Wang Becke95	13, 19, 53
TPSS1KCIS	13	2004	HMDFT	TPSS exchange KCIS	24, 25, 40, 46, 48, 59
MPW1KCIS	15	2004	HMDFT	modified Perdew−Wang KCIS	13, 24, 25, 40, this work
MPWKCIS1K	41	2004	HMDFT	modified Perdew−Wang KCIS	13, 24, 25, 40, this work

[a] *X* denotes the percentage of HF exchange in the functional. [b] Upper entry. [c] Lower entry.

BHs of HT reactions, and it is a subset of the previous BH42/04 database. The HTBH38/04 database is listed in the Supporting Information.

2.4. AE6 and Kinetics9 Benchmark Databases. We parametrized two new hybrid meta DFT methods, namely, MPW1KCIS and MPWKCIS1K (see Table 3), against the AE6 and Kinetics9 benchmark databases. AE6[69] is a database of atomization energies for six molecules. Kinetics9 is a database of three forward BHs, three reverse BHs, and three energies of reaction for the three reactions in the BH6 database.[69] We have previously used this training set to optimize the BB1K method.[50] The AE6 and Kinetics9 databases are listed in the Supporting Information.

The MPW1KCIS and MPWKCIS1K methods differ only in the value of *X*, which is the fraction of Hartree−Fock exchange. In MPW1KCIS, *X* is optimized to minimize the root-mean-square error (RMSE) for the AE6 database. In the MPWKCIS1K model, *X* was adjusted to minimize the RMSE for the Kinetics9 database. The optimized *X* parameters for the MPW1KCIS and MPWKCIS1K methods are given in Table 3.

2.5. Theoretical Methods Tested. We tested a number of DFT-type methods against the new database. In particular, we assessed 11 pure DFT or meta DFT methods: LSDA,[9,70] BP86,[4,5] BLYP,[5,6] BB95,[13] mPWLYP,[6,19] mPWKCIS,[19,24,25,40,46,48] mPWPW91,[19] TPSS,[46,48] TPSSKCIS,[24,25,40,46,48] and VSXC.[21] We tested 10 hybrid DFT methods: B3LYP,[6,11,12] B97-1,[22] B97-2,[35] B98,[20] BHandHLYP,[10] mPW1PW91,[19] MPW1K,[30] O3LYP,[32,33] PBE1PBE,[14] and X3LYP,[49] and we also assessed 8 hybrid meta DFT methods: B1B95,[13] BB1K,[50] MPW1B95,[53] MPWB1K,[53] MPW1KCIS, MPWKCIS1K, TPSS1KCIS,[24,25,40,46,48,59] and TPSSh.[46,48] All these DFT methods are summarized in Table 3.

Note that MPW1KCIS, MPWKCIS1K, TPSS1KCIS, and TPSSh are not the standard keywords of *Gaussian03*; the keywords required in *Gaussian03* to carry out the MPW1KCIS calculation are:

#MPWKCIS IOp(3/76 = 0850001500)

The keywords required in *Gaussian03* to carry out the MPWKCIS1K calculation are:

#MPWKCIS IOp(3/76 = 0590004100)

The keywords required in *Gaussian03* to carry out the TPSS1KCIS calculation are:

#TPSSKCIS IOp(3/76 = 0870001300)

The keywords required in *Gaussian03* to carry out the TPSSh calculation are:

#TPSSTPSS IOp(3/76 = 0900001000)

We also tested six ab initio WFT methods. They are the HF, MP2,[71] MP3,[72] MP4SDQ,[72] QCISD,[60] and QCISD(T)[60] methods.

2.6. Geometries, Basis Sets, and Spin−Orbit Energy. All W1 and DFT calculations were carried out using the *Gaussian03*[73] and MOLPRO[74] programs. Geometries for all molecules in this paper are optimized at the QCISD/MG3 level, where QCISD is quadratic configuration interaction with single and double excitations,[60] and MG3 is the modified[75,76] G3Large[77] basis set. It is also called the G3LargeMP2[76] basis set, which is the same as 6-311++G(3d2f,2df,2p)[78] for H−Si, but improved[77] for P−Ar. The 6-311++G(3d2f,2df,2p) basis set uses a single-ζ core and triple-ζ valence representation with additional diffuse functions on all atoms. The notation "(3d2f,2df,2p)" indicates three sets of d functions and two sets of f functions for second-row atoms, two sets of d functions and one set of f functions for first-row atoms, and two sets of p functions for hydrogen. The QCISD/MG3 geometries for molecules and saddle points in this paper can be obtained from the Truhlar group database website.[79] We tested all DFT methods in Table 3 with a recommended augmented polarized triple-ζ set, MG3S. The MG3S basis[42] is the same as MG3 except it omits diffuse functions on hydrogens.

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.[75]

TABLE 4: Mean Errors (kcal/mol) for the NHTBH38/04 Database[a,b]

	heavy atom-transfer (12)		NS[c] (16)		unimolecular and association (10)		total (38)	
methods	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE
Pure DFT or Meta DFT								
VSXC	−7.44	7.44	−5.30	5.30	−0.91	2.40	−4.26	4.67
BB95	−13.88	13.88	−6.36	6.36	−3.22	3.40	−7.42	7.47
mPWKCIS	−13.65	13.65	−6.66	6.66	−2.67	3.07	−7.39	7.50
TPSSKCIS	−13.37	13.37	−7.64	7.64	−2.56	2.98	−7.70	7.82
mPWPW91	−14.10	14.10	−7.45	7.45	−2.67	3.10	−7.90	8.02
PBE	−14.93	14.93	−6.97	6.97	−2.94	3.35	−8.00	8.11
BP86	−15.51	15.51	−6.91	6.91	−3.41	3.87	−8.32	8.45
TPSS	−14.65	14.65	−7.75	7.75	−3.84	4.04	−8.56	8.62
BLYP	−14.66	14.66	−8.40	8.40	−3.38	3.51	−8.65	8.69
mPWLYP	−15.76	15.76	−8.14	8.14	−3.64	3.79	−8.90	8.95
LSDA	−23.48	23.48	−8.50	8.50	−5.17	5.90	−11.84	12.05
Hybrid DFT								
MPW1K	−0.83	1.89	1.12	1.28	0.96	2.42	0.48	1.78
B97-2	−3.13	3.52	−1.43	1.47	0.62	1.91	−1.13	1.98
BHandHLYP	0.07	3.04	0.95	1.39	0.76	1.98	0.61	2.04
mPW1PW91	−5.99	5.99	−1.81	1.94	−0.38	2.00	−2.57	3.08
B98	−5.18	5.18	−2.96	2.96	−0.31	1.97	−2.66	3.12
B97-1	−5.18	5.18	−3.21	3.21	−0.23	1.83	−2.70	3.15
PBE1PBE	−6.62	6.62	−1.87	2.05	−0.58	2.16	−2.84	3.36
X3LYP	−8.48	8.48	−2.89	2.90	−1.43	2.06	−4.01	4.19
B3LYP	−8.49	8.49	−3.25	3.25	−1.42	2.02	−4.17	4.34
O3LYP	−8.27	8.27	2.61	4.42	−1.02	2.27	−1.46	4.94
Hybrid Meta DFT								
BB1K	−0.69	1.58	1.23	1.30	0.53	1.44	0.50	1.40
MPWB1K	−0.77	1.69	1.08	1.19	0.52	1.61	0.41	1.43
MPWKCIS1K	−0.77	1.97	0.92	1.17	0.91	2.05	0.43	1.66
B1B95	−4.73	4.73	−0.95	1.08	−0.58	1.21	−1.86	2.09
MPW1B95	−4.62	4.62	−0.81	1.21	−0.52	1.31	−1.75	2.14
MPW1KCIS	−8.64	8.64	−3.55	3.55	−1.21	1.96	−4.26	4.46
TPSS1KCIS	−9.26	9.26	−4.88	4.88	−1.39	2.12	−5.06	5.26
TPSSh	−11.51	11.51	−5.78	5.78	−2.94	3.23	−6.60	6.68
Ab initio WFT								
QCISD(T)	1.04	1.21	−0.62	1.08	0.30	0.53	0.13	0.96
QCISD	3.43	3.43	1.26	1.32	1.04	1.08	1.78	1.82
MP4SDQ	8.60	8.60	1.42	1.44	3.08	3.12	3.81	3.82
MP2	11.76	11.76	0.74	0.74	4.71	5.44	4.80	5.00
MP3	10.59	10.59	3.62	3.62	4.14	4.14	5.63	5.63
HF	14.86	16.87	6.67	6.67	2.70	3.82	7.91	8.90

[a] MUE denotes mean unsigned error. [b] MSE denotes mean signed error. [c] NS denotes nucleophilic substitution.

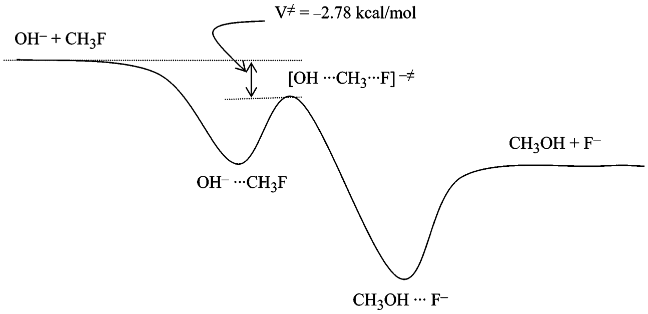

Figure 1. Energy profile along the reaction coordinate for the $OH^- + CH_3F$ S_N2 reaction. Note that the energy profile includes two wells corresponding to ion−molecule complexes, and the overall forward BH is negative.

3. Results and Discussion

3.1.W1 Results. Table 1 summarizes the W1 results for the 11 reactions. From this table, it can be seen that the HF calculations overestimate most of the BHs. The CCSD and (T) contributions tend to lower the BHs. The magnitudes of CCSD correlation contributions to the BHs are in a range from 1 to 32 kcal/mol. The magnitudes of (T) correlation contributions to the BHs are in a range from 0.5 to 8 kcal/mol. The contributions from core correlation and relativistic effects are much smaller than the CCSD and (T) contribution.

3.2. Benchmark Database of BHs for Non-HT Reactions. The new database is presented in Table 2. We will call this database NHTBH38/04. The magnitudes of the BHs are in the range −13 to +106 kcal/mol. Four of the BHs of S_N2 reactions are negative, which often results from the well-known[80,81] double-minimum shape of the energy profile (see Figure 1) for many S_N2 reactions. These overall negative BHs are well documented in the theoretical[63,67,82−85] and experimental[80,81,86−89] studies. There are 12 BHs for heavy-atom transfer reactions, 16 BHs for nucleophilic substitution (NS) reactions, and 10 BHs for non-NS unimolecular and association reaction.

3.3. Test of Theoretical Methods. The mean errors for the new database by the tested methods are listed in Table 4.

Table 4 shows that all 11 pure DFT and meta DFT methods systematically underestimate the BHs. Among these four methods, VSXC gives (by far) the best performance for calculating the BHs for non-HT reactions. This result is consistent with our analysis in a previous paper,[90] in which we concluded on the basis of a less diverse database that VSXC is the best pure or meta DFT method for thermochemistry and thermochemical kinetics.

TABLE 5: Mean Errors (kcal/mol) for the NHTBH38/04 and HTBH38/04 Databases

	non-HT (38)		HT (38)		total[a] (76)		weighted average	
methods	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE
				Pure DFT or Meta DFT				
VSXC	−4.26	4.67	−4.86	4.87	−4.56	4.77	−4.63	5.00
mPWKCIS	−7.39	7.50	−7.47	7.47	−7.43	7.49	−7.61	7.71
TPSSKCIS	−7.70	7.82	−7.01	7.01	−7.36	7.42	−7.65	7.75
BB95	−7.42	7.47	−8.14	8.14	−7.78	7.80	−7.90	7.94
mPWPW91	−7.90	8.02	−8.43	8.43	−8.17	8.23	−8.16	8.27
BLYP	−8.65	8.69	−7.52	7.52	−8.09	8.11	−8.49	8.52
TPSS	−8.56	8.62	−7.71	7.71	−8.14	8.17	−8.49	8.54
PBE	−8.00	8.11	−9.32	9.32	−8.66	8.71	−8.54	8.64
BP86	−8.32	8.45	−9.16	9.16	−8.74	8.81	−8.75	8.86
mPWLYP	−8.90	8.95	−8.56	8.56	−8.73	8.75	−9.03	9.06
LSDA	−11.84	12.05	−17.72	17.72	−14.78	14.88	−13.72	13.90
				Hybrid DFT				
MPW1K	0.48	1.78	−0.60	1.32	−0.06	1.55	0.16	1.73
BHandHLYP	0.61	2.04	0.95	2.73	0.78	2.38	0.68	2.28
B97-2	−1.13	1.98	−3.09	3.24	−2.11	2.61	−1.76	2.54
mPW1PW91	−2.57	3.08	−3.54	3.55	−3.06	3.32	−2.93	3.37
B98	−2.66	3.12	−4.16	4.16	−3.41	3.64	−3.15	3.57
B97-1	−2.70	3.15	−4.40	4.40	−3.55	3.77	−3.25	3.65
PBE1PBE	−2.84	3.36	−4.22	4.22	−3.53	3.79	−3.33	3.76
X3LYP	−4.01	4.19	−3.98	4.09	−3.99	4.14	−4.19	4.38
B3LYP	−4.17	4.34	−4.13	4.23	−4.15	4.28	−4.32	4.50
O3LYP	−1.46	4.94	−3.97	4.06	−2.72	4.50	−2.66	4.76
				Hybrid Meta DFT				
BB1K	0.50	1.40	−0.57	1.16	−0.03	1.28	0.13	1.37
MPWB1K	0.41	1.43	−0.85	1.29	−0.22	1.36	0.00	1.45
MPWKCIS1K	0.43	1.66	0.14	1.71	0.29	1.69	0.30	1.73
B1B95	−1.86	2.09	−2.80	2.80	−2.33	2.45	−2.27	2.45
MPW1B95	−1.75	2.14	−3.02	3.02	−2.38	2.58	−2.24	2.54
MPW1KCIS	−4.26	4.46	−4.39	4.41	−4.32	4.44	−4.45	4.64
TPSS1KCIS	−5.06	5.26	−4.69	4.69	−4.87	4.97	−5.06	5.24
TPSSh	−6.60	6.68	−5.97	5.97	−6.28	6.32	−6.55	6.62
				Ab initio WFT				
QCISD(T)	0.13	0.96	1.15	1.24	0.64	1.10	0.47	1.02
QCISD	1.78	1.82	2.73	2.81	2.25	2.31	2.11	2.16
MP4SDQ	3.81	3.82	3.89	3.89	3.85	3.86	4.25	4.26
MP2	4.80	5.00	3.69	4.14	4.24	4.57	5.23	5.52
MP3	5.63	5.63	4.44	4.44	5.04	5.04	5.70	5.70
HF	7.91	8.90	13.29	13.66	10.60	11.28	9.38	10.25

[a] This is calculated by using $^1/_4$ times MSE (or MUE) for heavy-atom transfer reaction BHs plus $^1/_4$ times MSE (or MUE) for S_N2 reaction BHs plus $^1/_4$ times MSE (or MUE) for unimolecular and association reaction BHs plus $^1/_4$ times MSE (or MUE) for HT reaction BHs.

Among the tested hybrid DFT methods, MPW1K gives the best performance for calculating the heavy-atom transfer reaction BHs and the S_N2 reaction BHs. B97-1 gives the lowest mean unsigned error (MUE) for the unimolecular and association reaction BHs. MPW1K is the best hybrid DFT method overall, and it gives the lowest MUE for all 38 BHs in the new database, with B97-2 only slightly behind.

Among the tested hybrid meta DFT methods, BB1K give the best performance for calculating the heavy-atom transfer reaction BHs. B1B95 gives the lowest MUE for the nucleophilic substitution reaction BHs and the unimolecular and association reaction BHs. BB1K and MPWB1K are the two best hybrid meta DFT methods in that they give lowest MUE for all 38 BHs in the new database.

Among the tested ab initio WFT methods, QCISD(T) gives the best performance for calculating the non-HT reaction BHs. HF, MP2, MP3, and MP4SDQ systematically overestimate the BHs as shown by their high mean signed error (MSE). Note that QCISD is outperformed by the BB1K, MPWB1K, MPWKCIS1K, and MPW1K methods even though it is *much* more computationally expensive.

We also calculated the BHs for the HTBH38/04 database for HT reaction BHs for all DFT methods included in this paper. The results for the HTBH38/04 database and for the new database are compared in Table 5. The quality of a DFT-type method for calculating HT reaction BHs is found to correlate well with its quality for calculating non-HT reaction BHs.

Table 5 also gives the overall mean errors for the combined 76 BHs. To check whether our conclusions are a strong function of the number of each kind of reaction, we also computed weighted mean errors in which each of the four kinds of reaction is weighted by $^1/_4$. Table 5 shows that the conclusions from the weighted mean errors are exactly the same as from the overall mean errors. These conclusions are given in Section 4.

3.4. Analytical Remarks. Although the purpose of this paper is to provide tests, and possibly validations, of density functionals against carefully prepared benchmark data on reactions and not to analyze the functionals theoretically, it is useful to add a few comments on theoretical analysis. The theoretical grounds for admixing Hartree−Fock exchange with GGAs were provided by Becke.[11] In brief, the GGAs work better for short-range electron correlation holes, and Hartree−Fock exchange works better for long-range ones. The reason the optimum fraction of Hartree−Fock exchange is less than one-half has been discussed by Perdew et al.[15] In addition, the density functional exchange builds in effects that are commonly called static correlation in WFT.[7,18] As a result of these considerations, the optimum amount of Hartree−Fock exchange depends on the molecule or reaction, depends on the property of interest for that molecule or reaction, and, since different GGAs are designed for different purposes, or at least in different ways, also depends on the choice of GGA. For example, some density functionals, such as B1B95, PBE1PBE, TPSS, and TPSSh, build in the exact uniform density limit,[13,14,48] whereas others do not, and meta density functionals can eliminate the incorrect attribution of electron correlation effects to one-electron regions. The former property is probably more important in metals than in the BHs considered here, whereas the latter is clearly more important in organic chemistry, with its plethora of hydrogen atoms, than in metals. Tables 3 and 5 show that more than about 40% of HF exchange is needed for hybrid meta DFT or hybrid DFT methods to obtain accurate BHs, as exemplified by the good performance of the BB1K, MPWB1K, MPWKCIS1K, and MPW1K methods. Note that two DFT methods based on nonempirical functionals, namely, TPSS1KCIS and TPSSh, do poorly for BH calculations because the percentage of HF exchange in the canonical versions of both methods is small (13 and 10%, respectively).

4. Concluding Remarks

In this paper, we developed a benchmark database of forward and reverse BHs for 19 non-HT reactions. We tested 29 DFT methods and 6 WFT methods against the new database and also against a combined database of 38 HT and 38 non-HT BHs. Among the tested pure DFT and meta DFT methods, VSXC[21] give the best performance for the calculations of BHs, with a MUE of 4.9 kcal/mol. Among the tested hybrid DFT methods, MPW1K[30] is the most accurate model for calculations of BHs, with a mean unsigned error of 1.6 kcal/mol. The very popular B3LYP[5,6,12] method has a MUE of 4.4 kcal/mol for the same database and systematically underestimates BHs.[30] Among the tested hybrid meta DFT methods, BB1K[50] and MPWB1K[53] are the two most accurate models for the calculations of BHs, with MUEs of 1.3 and 1.4 kcal/mol, respectively. Some other methods with MUEs below 3.5 kcal/mol are MPWKCIS1K (1.7 kcal/mol), B1B95[13] (2.5 kcal/ mol), MPW1B95[53] (2.5 kcal/mol), B97−2[35] (2.5 kcal/mol), and mPW1PW91[19] (3.4 kcal/mol). When using the results of this paper, the reader must ultimately consider more than just the performance of the methods for BHs. For example, we pointed out previously[30] that, although BHandHLYP has a reasonably low MUE for BHs, it is far less accurate than methods such as MPW1K and mPW1PW91 for energies of reaction, and for that reason (and others), it cannot be recommended for most applications.

Overall, BB1K and MPWB1K are the two best DFT methods for calculating BHs, whereas QCISD(T) is the best ab initio WFT method for BH calculations, and QCISD is second best, but QCISD is outperformed by the BB1K, MPWB1K, MPWKCIS1K, and MPW1K methods.

Our databases are now much broader than previous kinetics databases for testing electronic structure theory, and this improves our confidence in the conclusions of the present validation study.

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Supporting Information Available: The HTBH38/04 database and the calculated BHs 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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