Supporting Information: Representative Benchmark Suites for Barrier Heights of Diverse Reaction Types and Assessment of Electronic Structure Methods for Thermochemical Kinetics

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Prepared for *J. Chem. Theory Comput.*

November 7, 2006

Number of pages: 11

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Table S1: Benchmark Database NHTBH38/04.

Reactions	Barrier($V_f^{\neq}/V_r^{\neq}$)[a]
Heavy-Atom Transfer Reactions (HAT)	
$H + N_2O \longrightarrow OH + N_2$	18.14/83.22
$H + FH \longrightarrow HF + H$	42.18/42.18
$H + ClH \longrightarrow HCl + H$	18.00/18.00
$H + FCH_3 \longrightarrow HF + CH_3$	30.38/57.02
$H + F_2 \longrightarrow HF + F$	2.27/106.18
$CH_3 + FCl \longrightarrow CH_3F + Cl$	7.43/61.01
Nucleophilic Substitution Reactions (NS)	
$F^- + CH_3F \longrightarrow FCH_3 + F^-$	-0.34/-0.34
$F^-\cdots CH_3F \longrightarrow FCH_3\cdots F^-$	13.38/13.38
$Cl^- + CH_3Cl \longrightarrow ClCH_3 + Cl^-$	3.10/3.10
$Cl^-\cdots CH_3Cl \longrightarrow ClCH_3\cdots Cl^-$	13.61/13.61
$F^- + CH_3Cl \longrightarrow FCH_3 + Cl^-$	-12.54/20.11
$F^-\cdots CH_3Cl \longrightarrow FCH_3\cdots Cl^-$	2.89/29.62
$OH^- + CH_3F \longrightarrow HOCH_3 + F^-$	-2.78/17.33
$OH^-\cdots CH_3F \longrightarrow HOCH_3\cdots F^-$	10.96/47.20
Unimolecular and Association Reactions (UA)	
$H + N_2 \longrightarrow HN_2$	14.69/10.72
$H + CO \longrightarrow HCO$	3.17/22.68
$H + C_2H_4 \longrightarrow CH_3CH_2$	1.72/41.75
$CH_3 + C_2H_4 \longrightarrow CH_3CH_2CH_2$	6.85/32.97
$HCN \longrightarrow HNC$	48.16/33.11

[a] $V_f^{\neq}$ denotes forward BH, and $V_r^{\neq}$ denotes reverse BH (in kcal/mol).

Table S2: Calculated errors for representative data sets of non-hydrogen transfer reactions and costs of methods that are in Table 1 but not in Table 3.

Methods	HATBH6		NSBH6		UABH6		
	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]
			N^7 Methods				
MLSE4+d	−0.66	1.73	−3.89	4.76	−0.25	0.39	2.29
MLSE3+d	−0.04	1.35	−4.02	4.91	−0.13	0.33	2.20
MLSE2+d	−0.68	1.61	−4.39	5.83	−0.28	0.49	2.64
MLSE1+d	−0.35	1.22	−4.74	6.06	−0.26	0.36	2.55
QCISD(T)/cc-pV(D+d)Z	2.02	2.98	−3.90	7.53	−0.02	1.45	3.99
MP4/6-31+G(d)	9.43	9.43	−0.37	2.34	3.84	4.78	5.52
MP4/6-31G(2df,p)	7.58	7.58	−4.23	9.14	4.09	4.38	7.03
			N^6 Methods				
CCSD/aug-cc-pVTZ	3.15	3.15	1.66	1.66	0.81	0.89	1.90
CCSD/6-31+G(d,p)	5.10	5.53	2.12	2.24	2.08	2.08	3.28
MP4SDQ/aug-cc-pVTZ	7.40	7.40	1.16	1.16	2.67	2.67	3.74
CCSD/6-31+B(d,p)	3.95	6.56	1.66	2.54	2.37	2.37	3.82
MP3/aug-cc-pVTZ	9.16	9.16	2.93	2.93	3.75	3.75	5.28
MP4SDQ/6-31+B(d,p)	8.12	8.95	1.17	2.63	4.37	4.37	5.32
MP4SDQ/6-31+G(p,d)	9.70	9.70	1.59	2.19	4.15	4.15	5.35
MP4SDQ/cc-pV(D+d)Z	8.79	8.79	−1.98	6.99	2.78	3.33	6.37
MP3/6-31+B(d,p)	9.82	10.12	3.37	3.59	5.42	5.42	6.38
MP3/6-31+G(d,p)	11.36	11.36	3.80	3.80	5.17	5.17	6.78
MP3/6-31G(2df,p)	10.13	10.13	−0.28	7.27	5.24	5.24	7.55

Table S2: Continued.

Methods	HATBH6		NSBH6		UABH6		
	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]
			N^5 Methods				
MP2/aug-cc-pV(D+d)Z	9.73	9.73	−0.48	1.00	4.06	4.96	5.23
MP2/aug-cc-pVTZ	10.05	10.05	0.44	0.80	4.57	5.43	5.43
MP2/6-31++G(2df,2pd)	10.29	10.29	0.53	0.70	4.96	5.73	5.57
MP2/6-311++G(2df,2pd)	10.29	10.29	0.53	0.70	4.96	5.73	5.57
MP2/MG3	10.74	10.74	0.73	0.81	5.03	5.96	5.84
MP2/6-31+B(d,p)	10.48	10.48	0.79	3.01	5.97	6.29	6.59
MP2/cc-pV(T+d)Z	10.91	10.91	−1.99	4.58	4.78	5.77	7.09
MP2/6-311++G(d,p)	12.28	12.28	3.23	3.23	5.01	6.25	7.25
MP2/6-311+G(d,p)	12.28	12.28	3.23	3.23	5.01	6.25	7.25
MP2/6-31+G(d)	12.70	12.70	1.48	2.72	5.88	7.35	7.59
MP2/cc-pV(D+d)Z	11.45	11.45	−2.32	7.34	4.43	5.91	8.23
MP2/cc-pVDZ	11.68	11.68	−2.56	7.27	4.43	5.91	8.29
SAC-MP2/6-31G(d)	12.09	13.42	−2.77	9.05	6.62	9.19	10.55
			N^4 Methods				
PWB6K/aug-pc2	−0.32	0.75	1.49	1.49	0.54	1.58	1.27
B98/6-311+G(3df,2p)	−5.57	5.57	−2.96	−2.96	−0.16	1.83	1.48
τHCTHh/MG3S	−9.83	9.83	−6.01	6.01	−0.71	2.09	5.98
B3LYP*/MG3T	−6.44	6.44	−6.73	8.13	1.94	4.82	6.46
TPSSh/MG3S	−10.75	10.75	−5.82	5.82	−2.94	2.94	6.50
B3LYP/6-311G(2df,2p)	−7.95	7.95	−8.81	11.35	−1.58	1.75	7.02

Table S2: Continued.

Methods	HATBH6		NSBH6		UABH6		
	MSE	MUE	MSE	MUE	MSE	MUE	MMUE[a]
B3LYP/6-311G(2d,p)	−7.96	7.96	−9.41	11.83	−1.81	1.82	7.20
B3LYP/6-31G(d,p)	−8.56	8.56	−8.97	13.02	−1.45	2.36	7.98
HF/cc-pV(D+d)Z	16.61	16.61	1.56	4.78	2.92	3.26	8.22
HF/cc-pVDZ	16.74	16.74	1.26	4.71	2.92	3.26	8.24
BB1K/MIDIY	−6.46	6.46	−11.13	16.86	0.80	1.85	8.39
HF/cc-pV(T+d)Z	17.52	17.52	4.07	4.41	3.28	3.48	8.47
HF/aug-cc-pV(D+d)Z	16.92	16.92	5.27	5.27	2.90	3.48	8.56
HF/6-31+B(d,p)	16.29	16.68	5.20	5.20	4.21	4.21	8.70
HF/6-31+G(d,2p)	17.46	17.46	5.58	5.58	3.69	3.91	8.98
HF/aug-cc-pVTZ	17.36	17.36	6.44	6.44	3.25	3.51	9.10
HF/MG3	17.52	17.52	6.36	6.36	3.48	3.58	9.15
HF/G3XLarge	17.47	17.47	6.42	6.42	3.48	3.57	9.15
HF/6-31B(d)	18.02	18.43	3.69	6.50	4.70	4.70	9.88
			N^3 Methods				
PBE1W/MG3S	−13.77	13.77	−7.30	7.30	−2.52	2.56	7.88
PW91/MG3S	−14.78	14.78	−7.92	7.92	−2.62	2.63	8.44

[a] MMUE is defined by Eq. 4.

Table S3: QCISD/MG3 geometries (Cartesian coordinates) for DBH24 database (in Å).

	C_2H_4 (charge=0, spin=1)		
C	0.000000	0.000000	0.665593
C	0.000000	0.000000	−0.665593
H	0.000000	0.921495	1.231668
H	0.000000	−0.921495	1.231668
H	0.000000	0.921495	−1.231668
H	0.000000	−0.921495	−1.231668
	CH_3 (charge=0, spin=2)		
C	0.000000	0.000000	0.000000
H	1.077317	0.000000	0.000000
H	−0.538659	0.932984	0.000000
H	−0.538659	−0.932984	0.000000
	CH_3CH_2 (charge=0, spin=2)		
C	−0.258719	−0.816829	0.000000
C	−0.250987	0.674191	0.000000
H	0.758830	−1.225939	0.000000
H	−0.758830	−1.213866	0.883419
H	−0.758830	−1.213866	−0.883419
H	−0.170021	1.225939	−0.924320
H	−0.170021	1.225939	0.924320
	CH_3F (charge=0, spin=1)		
C	−0.632074	0.000001	−0.000000
F	0.749117	0.000002	−0.000002
H	−0.983182	−0.338489	0.972625
H	−0.983222	1.011553	−0.193172
H	−0.983203	−0.673084	−0.779437
	CH_3OH (charge=0, spin=1)		
C	−0.046423	0.663069	0.000000
O	−0.046423	−0.755063	0.000000
H	−1.086956	0.975938	0.000000
H	0.860592	−1.057039	0.000000
H	0.438145	1.071594	0.889539
H	0.438145	1.071594	−0.889539
	CH_4 (charge=0, spin=1)		
C	0.000000	0.000000	0.000000
H	0.627837	0.627837	0.627837
H	−0.627837	−0.627837	0.627837
H	0.627837	−0.627837	−0.627837
H	−0.627837	0.627837	−0.627837

Table S3: Continued.

	$Cl^{-}\cdots CH_3Cl$ (charge=-1, spin=1)		
Cl	0.000000	0.000000	−2.384735
C	0.000000	0.000000	−0.566331
H	0.000000	1.025066	−0.224379
H	−0.887734	−0.512533	−0.224379
H	0.887734	−0.512533	−0.224379
Cl	0.000000	0.000000	2.624213
	FCl (charge=0, spin=1)		
F	0.000000	0.000000	−1.065985
Cl	0.000000	0.000000	0.564345
	$FCH_3\cdots Cl^{-}$ (charge=-1, spin=1)		
F	0.000000	0.000000	−2.648539
C	0.000000	0.000000	−1.240170
H	0.000000	1.024719	−0.886406
H	−0.887432	−0.512359	−0.886406
H	0.887432	−0.512359	−0.886406
Cl	0.000000	0.000000	1.996299
	$F^{-}\cdots CH_3Cl$ (charge=-1, spin=1)		
Cl	0.000000	0.000000	1.623138
C	0.000000	0.000000	−0.227358
H	0.000000	1.026321	−0.555141
H	0.888820	−0.513160	−0.555141
H	−0.888820	−0.513160	−0.555141
F	0.000000	0.000000	−2.729308
	H_2 (charge=0, spin=1)		
H	0.000000	0.000000	0.370938
H	0.000000	0.000000	−0.370938
	HCl (charge=0, spin=1)		
H	0.000000	0.000000	−1.203645
Cl	0.000000	0.000000	0.070803
	HCN (charge=0, spin=1)		
C	0.000000	0.000000	−0.500365
N	0.000000	0.000000	0.652640
H	0.000000	0.000000	−1.566291
	HN_2 (charge=0, spin=2)		
N	−0.062442	0.659491	0.000000
N	−0.062442	−0.518709	0.000000
H	0.874194	−0.985478	0.000000
	HNC (charge=0, spin=1)		
C	0.000000	0.000000	−0.737248
N	0.000000	0.000000	0.432089
H	0.000000	0.000000	1.426960

Table S3: Continued.

	H_2O (charge=0, spin=1)		
O	0.000000	0.000000	0.117145
H	0.000000	0.756709	−0.468582
H	0.000000	−0.756709	−0.468582
	H_2S (charge=0, spin=1)		
S	0.000000	0.000000	0.102519
H	0.000000	0.966249	−0.820154
H	0.000000	−0.966249	−0.820154
	HS (charge=0, spin=2)		
S	0.000000	0.000000	0.078835
H	0.000000	0.000000	−1.261367
	N_2 (charge=0, spin=1)		
N	0.000000	0.000000	0.548555
N	0.000000	0.000000	−0.548555
	N_2O (charge=0, spin=1)		
N	0.000000	0.000000	−1.195674
N	0.000000	0.000000	−0.075111
O	0.000000	0.000000	1.111937
	OH (charge=0, spin=2)		
O	0.000000	0.000000	0.107655
H	0.000000	0.000000	−0.861243
	OH^- (charge=-1, spin=1)		
O	0.000000	0.000000	0.106894
H	0.000000	0.000000	−0.855149
	O (charge=0, spin=3)		
O	0.000000	0.000000	0.000000
	$H + N_2O \longrightarrow OH + N_2$ saddle point (charge=0, spin=2)		
H	−0.303286	−1.930712	0.000000
O	−0.861006	−0.621526	0.000000
N	0.000000	0.257027	0.000000
N	1.027333	0.729104	0.000000
	$H + ClH \longrightarrow HCl + H$ saddle point (charge=0, spin=2)		
H	0.000000	0.000000	1.485800
Cl	0.000000	0.000000	0.000000
H	0.000000	0.000000	−1.485800
	$CH_3 + FCl \longrightarrow CH_3F + Cl$ saddle point (charge=0, spin=2)		
Cl	1.454749	−0.001237	−0.000040
F	−0.323587	0.004631	0.000124
C	−2.387418	−0.002147	−0.000073
H	−2.495086	−0.855361	−0.649404
H	−2.497313	−0.138673	1.063139
H	−2.501537	0.986269	−0.413734

Table S3: Continued.

	$Cl^- \cdots CH_3Cl \longrightarrow ClCH_3 \cdots Cl^-$ saddle point (charge=-1, spin=1)		
Cl	0.000025	0.019526	2.322499
C	0.000513	0.000486	−0.000089
H	0.761278	−0.750733	0.006377
H	−1.030451	−0.282724	0.002147
H	0.270728	1.034927	−0.008697
Cl	−0.000297	−0.019784	−2.322458
	$F^- \cdots CH_3Cl \longrightarrow FCH_3 \cdots Cl^-$ saddle point (charge=-1, spin=1)		
F	0.000000	0.000000	−2.537929
C	0.000000	0.000000	−0.488372
H	1.062087	0.000000	−0.614972
H	−0.531044	0.919794	−0.614972
H	−0.531044	−0.919794	−0.614972
Cl	0.000000	0.000000	1.624501
	$OH^- + CH_3F \longrightarrow HOCH_3 + F^-$ saddle point (charge=-1, spin=1)		
F	1.850614	−0.013179	−0.000128
C	0.090857	0.010586	0.000269
H	0.040907	1.079548	−0.011749
H	0.037163	−0.528013	−0.922944
H	0.037486	−0.507463	0.935132
O	−1.892801	0.103266	−0.000118
H	−2.173821	−0.815112	0.000039
	$H + N_2 \longrightarrow HN_2$ saddle point (charge=0, spin=2)		
N	0.084563	−0.642934	0.000000
N	0.084563	0.479877	0.000000
H	−1.183883	1.141399	0.000000
	$H + C_2H_4 \longrightarrow CH_3CH_2$ saddle point (charge=0, spin=2)		
C	−0.567877	0.000051	−0.218958
C	0.751139	−0.000036	0.041932
H	−1.493884	−0.000488	1.531765
H	−1.101691	0.920651	−0.408626
H	−1.102022	−0.920234	−0.409110
H	1.299128	−0.922344	0.173763
H	1.298899	0.922325	0.174363
	HCN $\longrightarrow$ HNC saddle point (charge=0, spin=1)		
C	0.080319	0.620258	0.000000
N	0.080319	−0.568095	0.000000
H	−1.044148	0.255121	0.000000

Table S3: Continued.

	$OH + CH_4 \longrightarrow CH_3 + H_2O$ saddle point (charge=0, spin=2)		
C	−1.211487	0.007968	0.000407
O	1.293965	−0.108694	0.000133
H	0.009476	−0.118020	0.002799
H	−1.525529	−0.233250	1.010070
H	−1.430665	1.033233	−0.278082
H	−1.552710	−0.710114	−0.737702
H	1.416636	0.849894	−0.000591
	$H + OH \longrightarrow O + H_2$ saddle point (charge=0, spin=3)		
H	0.000000	0.000000	−0.860287
O	0.000000	0.000000	0.329024
H	0.000000	0.000000	−1.771905
	$H + H_2S \longrightarrow H_2 + HS$ saddle point (charge=0, spin=2)		
H	1.262097	−0.220097	0.000000
S	0.000000	0.223153	0.000000
H	−0.500576	−1.115445	0.000000
H	−0.761521	−2.234913	0.000000

Table S4: Geometry of phosphinomethanol (Cartesian coordinates, in Å).

	PH_2CH_2OH (charge=0, spin=1)		
C	0.228522	0.352270	0.000000
P	0.228522	−1.513230	0.000000
O	0.765122	0.708370	−0.879900
H	−0.769078	0.788470	0.000000
H	0.765122	0.708370	0.879900
H	−0.710678	−1.700330	−1.038000
H	−0.710678	−1.700330	1.038000
H	0.769078	1.700330	−0.886386

Table S5: T1 diagnostic values[a] of the species in DBH24.

C_2H_4	0.0108	CH_3	0.0055	CH_3CH_2	0.0102
CH_3F	0.0103	CH_3OH	0.0099	CH_4	0.0075
$Cl^-\cdots CH_3Cl$	0.0083	FCl	0.0123	$FCH_3\cdots Cl$	0.0096
$F^-\cdots CH_3Cl$	0.0150	H	0.0000	H_2	0.0053
HCl	0.0061	HCN	0.0142	HN_2	0.0276
HNC	0.0163	H_2O	0.0010	H_2S	0.0098
HS	0.0075	N_2	0.0131	N_2O	0.0197
OH	0.0091	OH^-	0.0219	O	0.0058
$H + N_2O \longrightarrow OH + N_2$ saddle point					0.0349
$H + ClH \longrightarrow HCl + H$ saddle point					0.0070
$CH_3 + FCl \longrightarrow CH_3F + Cl$ saddle point					0.0619
$Cl^-\cdots CH_3Cl \longrightarrow ClCH_3\cdots Cl^-$ saddle point					0.0167
$F^-\cdots CH_3Cl \longrightarrow FCH_3\cdots Cl^-$ saddle point					0.0183
$OH^- + CH_3F \longrightarrow HOCH_3 + F^-$ saddle point					0.0201
$H + N_2 \longrightarrow HN_2$ saddle point					0.0237
$H + C_2H_4 \longrightarrow CH_3CH_2$ saddle point					0.0197
$HCN \longrightarrow HNC$ saddle point					0.0269
$OH + CH_4 \longrightarrow CH_3 + H_2O$ saddle point					0.0314
$H + OH \longrightarrow O + H_2$ saddle point					0.0328
$H + H_2S \longrightarrow H_2 + HS$ saddle point					0.0098

[a] CCSD(T)/aug-cc-pVTZ.