Supporting Information for:

Benchmark Database of Barrier Heights for Heavy Atom Transfer, Nucleophilic Substitution, Association, and Unimolecular Reactions and its Use to Test Density Functional Theory

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Table S1: HTBH38/04 Database[a]

Reaction	best estimate	
A + BC → AB + C	$V_f^{\neq}$	$V_r^{\neq}$
1. H + HCl → H_2 + Cl	5.7	8.7
2. OH + H_2 → H + H_2O	5.1	21.2
3. CH_3 + H_2 → H + CH_4	12.1	15.3
4. OH + CH_4 → CH_3 + H_2O	6.7	19.6
5. H + H_2 → H_2 + H	9.6	9.6
6. OH + NH_3 → H_2O + NH_2	3.2	12.7
7. HCl + CH_3 → Cl + CH_4	1.7	7.9
8. OH + C_2H_6 →H_2O + C_2H_5	3.4	19.9
9. F + H_2 → HF + H	1.8	33.4
10. O + CH_4 →OH + CH_3	13.7	8.1
11. H + PH_3→ PH_2 + H_2	3.1	23.2
12. H + HO → H_2 +O	10.7	13.1
13. H + H_2S → H_2 + HS	3.5	17.3
14. O + HCl → OH + Cl	9.8	10.4
15. NH_2 + CH_3→ CH_4 + NH	8.0	22.4
16. NH_2 + C_2H_5 → C_2H_6 + NH	7.5	18.3
17. C_2H_6 + NH_2 → NH_3 + C_2H_5	10.4	17.4
18. NH_2 + CH_4 → CH_3 + NH_3	14.5	17.8
19. *s-trans cis*-C_5H_8 → *s-trans cis*-C_5H_8	38.4	38.4

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

Table S2: Barrier Heights Calculated by Pure or Meta DFT Methods[a,b]

Reactions		VSXC	BB95	mPWPW91	TPSS	BLYP	LSDA	BP86	TPSSKCIS	PBE	mPWLYP	mPWKCIS
Heavy atom transfer reactions												
$H + N_2O \rightarrow OH + N_2$	$V_f^{\neq}$	16.02	11.65	10.77	8.41	8.94	3.16	8.10	10.97	10.46	8.13	10.39
	$V_r^{\neq}$	71.18	55.36	55.34	60.37	61.78	32.20	55.87	60.62	52.64	59.91	59.30
$H + FH \rightarrow HF + H$	$V_f^{\neq}$	36.75	29.71	28.57	27.33	26.77	19.40	26.00	29.15	27.98	25.94	28.59
	$V_r^{\neq}$	36.75	29.71	28.57	27.33	26.77	19.40	26.00	29.15	27.98	25.94	28.59
$H + ClH \rightarrow HCl + H$	$V_f^{\neq}$	17.40	12.25	10.92	8.21	10.57	3.02	8.41	11.59	10.45	10.01	11.38
	$V_r^{\neq}$	17.40	12.25	10.92	8.21	10.57	3.02	8.41	11.59	10.45	10.01	11.38
$H + FCH_3 \rightarrow HF + CH_3$	$V_f^{\neq}$	21.79	19.78	18.94	17.35	16.33	13.62	16.25	18.98	18.74	15.56	18.04
	$V_r^{\neq}$	51.65	41.88	42.48	42.17	42.33	31.78	42.55	42.43	41.14	40.62	43.75
$H + F_2 \rightarrow HF + F$	$V_f^{\neq}$	-6.98	-8.87	-9.41	-10.72	-11.49	-15.75	-11.15	-9.10	-9.63	-12.30	-9.99
	$V_r^{\neq}$	96.18	80.73	81.92	82.97	81.63	68.95	82.24	82.81	80.34	79.90	83.16
$CH_3 + FCl \rightarrow CH_3F + Cl$	$V_f^{\neq}$	-6.99	-6.23	-5.68	-5.35	-6.94	-11.47	-5.87	-5.95	-6.42	-8.33	-5.85
	$V_r^{\neq}$	45.59	41.23	43.44	43.93	42.80	36.87	43.05	43.36	42.71	41.52	43.44
Nucleophilic substitution reactions												
$F^- + CH_3F \rightarrow FCH_3 + F^-$	$V_f^{\neq}$	-7.63	-6.76	-7.74	-8.93	-7.88	-12.17	-7.57	-8.74	-8.33	-9.48	-7.35
	$V_r^{\neq}$	-7.63	-6.76	-7.74	-8.93	-7.88	-12.17	-7.57	-8.74	-8.33	-9.48	-7.35
$F^-\cdots CH_3F \rightarrow FCH_3 \cdots F^-$	$V_f^{\neq}$	12.00	6.94	6.53	5.74	6.11	6.28	6.34	5.95	6.66	5.88	6.74
	$V_r^{\neq}$	12.00	6.94	6.53	5.74	6.11	6.28	6.34	5.95	6.66	5.88	6.74
$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	$V_f^{\neq}$	-4.09	-2.59	-3.37	-5.09	-3.88	-6.67	-3.62	-4.52	-3.74	-5.05	-3.18
	$V_r^{\neq}$	-4.09	-2.59	-3.37	-5.09	-3.88	-6.67	-3.62	-4.52	-3.74	-5.05	-3.18
$Cl^-\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$	$V_f^{\neq}$	10.83	6.79	6.63	5.26	5.55	6.54	6.13	5.74	6.92	5.40	6.62
	$V_r^{\neq}$	10.83	6.79	6.63	5.26	5.55	6.54	6.13	5.74	6.92	5.40	6.62

$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	$V_f^{\neq}$	-20.29	-17.99	-22.65	-21.14	-24.24	-23.34	-19.17	-20.48	-19.52	-20.73	-18.63
	$V_r^{\neq}$	12.96	13.38	8.95	13.44	7.97	9.81	13.17	13.17	12.10	11.55	13.00
$F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$	$V_f^{\neq}$	-4.35	-1.38	-0.23	-0.33	-4.27	-1.24	-1.63	-2.23	-0.98	-2.04	-1.21
	$V_r^{\neq}$	26.59	21.17	17.25	21.99	15.80	21.19	21.14	21.74	21.04	20.42	21.20
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	$V_f^{\neq}$	-9.58	-8.91	-10.11	-10.84	-9.78	-14.47	-9.65	-10.69	-10.67	-11.41	-9.58
	$V_r^{\neq}$	10.53	10.86	10.22	8.35	9.59	6.21	10.03	8.61	9.63	8.02	10.46
$OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$	$V_f^{\neq}$	10.19	3.79	3.17	2.78	3.20	3.05	3.22	3.01	3.37	2.97	3.56
	$V_r^{\neq}$	39.20	40.93	42.39	40.02	39.80	47.14	42.02	40.00	42.72	39.72	41.32
Unimolecular and Association Reaction												
$H + N_2 \rightarrow HN_2$	$V_f^{\neq}$	10.27	7.28	5.88	3.27	5.59	-1.85	3.43	6.34	5.57	5.04	6.08
	$V_r^{\neq}$	11.88	8.64	9.36	8.51	8.58	9.53	9.47	9.15	9.23	8.64	9.37
$H + CO \rightarrow HCO$	$V_f^{\neq}$	2.15	-0.49	-1.40	-4.98	-1.93	-7.56	-3.37	-1.49	-1.69	-2.39	-1.41
	$V_r^{\neq}$	26.23	23.56	24.82	23.71	23.36	26.36	24.99	24.77	24.72	23.45	24.66
$H + C_2H_4 \rightarrow CH_3CH_2$	$V_f^{\neq}$	2.66	0.87	0.19	-4.17	-0.61	-5.24	-1.89	-0.29	-0.04	-1.06	0.00
	$V_r^{\neq}$	43.38	37.71	40.72	40.02	38.29	39.40	40.93	40.90	40.39	38.17	40.40
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	$V_f^{\neq}$	3.96	3.00	2.69	3.31	4.75	-5.72	2.69	3.54	1.57	3.41	4.01
	$V_r^{\neq}$	25.36	26.56	29.15	27.84	24.88	32.97	28.47	27.37	29.72	25.05	27.25
$HCN \rightarrow HNC$	$V_f^{\neq}$	47.52	45.67	46.33	47.65	47.04	45.16	45.83	47.72	45.95	47.00	46.95
	$V_r^{\neq}$	33.30	30.77	31.33	32.31	32.10	31.08	31.14	32.17	30.97	32.12	31.78

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

[b] MG3S basis set and QCISD/MG3 geometries are used for all calculations in this table.

Table S3: Barrier Heights Calculated by Hybrid DFT Methods[a,b]

Reactions		MPW1K	B97-2	BHandHLYP	mPW1PW91	B98	B97-1	PBE1PBE	X3LYP	B3LYP	O3LYP
Heavy-atom transfer reactions											
$H + N_2O \rightarrow OH + N_2$	$V_f^{\neq}$	17.16	18.69	16.08	14.65	15.43	16.37	14.44	11.74	11.81	12.65
	$V_r^{\neq}$	81.63	72.36	91.27	71.24	74.10	72.62	68.97	73.01	72.92	66.93
$H + FH \rightarrow HF + H$	$V_f^{\neq}$	39.72	41.01	39.28	35.17	38.10	38.91	34.71	31.79	31.83	32.45
	$V_r^{\neq}$	39.72	41.01	39.28	35.17	38.10	38.91	34.71	31.79	31.83	32.45
$H + ClH \rightarrow HCl + H$	$V_f^{\neq}$	16.85	18.90	17.30	14.54	16.14	17.02	14.16	13.14	13.17	12.47
	$V_r^{\neq}$	16.85	18.90	17.30	14.54	16.14	17.02	14.16	13.14	13.17	12.47
$H + FCH_3 \rightarrow HF + CH_3$	$V_f^{\neq}$	30.90	29.76	30.03	26.07	27.03	27.77	25.96	22.20	22.03	22.66
	$V_r^{\neq}$	56.53	52.46	57.50	50.94	50.84	49.83	49.92	48.35	48.71	51.14
$H + F_2 \rightarrow HF + F$	$V_f^{\neq}$	-2.21	-0.57	-4.21	-4.24	-2.72	-2.13	-4.32	-7.32	-7.32	-6.25
	$V_r^{\neq}$	110.28	101.10	112.76	99.61	99.04	97.50	98.41	95.79	95.57	96.40
$CH_3 + FCl \rightarrow CH_3F + Cl$	$V_f^{\neq}$	5.83	-0.07	5.71	1.35	-1.35	-2.06	0.84	-1.66	-1.55	0.38
	$V_r^{\neq}$	62.74	54.92	64.51	55.10	52.99	52.10	54.56	52.24	52.00	53.03
Nucleophilic substitution reactions											
$F^- + CH_3F \rightarrow FCH_3 + F^-$	$V_f^{\neq}$	0.67	-1.50	0.33	-2.36	-3.32	-3.84	-2.71	-4.25	-3.94	-0.56
	$V_r^{\neq}$	0.67	-1.50	0.33	-2.36	-3.32	-3.84	-2.71	-4.25	-3.94	-0.56
$F^-\cdots CH_3F \rightarrow FCH_3 \cdots F^-$	$V_f^{\neq}$	14.18	11.42	14.47	11.27	10.72	10.53	11.43	10.16	9.98	10.87
	$V_r^{\neq}$	14.18	11.42	14.47	11.27	10.72	10.53	11.43	10.16	9.98	10.87
$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	$V_f^{\neq}$	3.64	1.63	3.09	1.12	-0.85	-0.95	0.88	-0.73	-0.53	3.38
	$V_r^{\neq}$	3.64	1.63	3.09	1.12	-0.85	-0.95	0.88	-0.73	-0.53	3.38
$Cl^-\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$	$V_f^{\neq}$	13.30	10.91	12.85	10.79	9.47	9.65	11.05	9.21	9.03	11.10
	$V_r^{\neq}$	13.30	10.91	12.85	10.79	9.47	9.65	11.05	9.21	9.03	11.10

$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	$V_f^{\neq}$	-13.10	-14.39	-14.01	-15.05	-16.77	-16.88	-15.43	-14.65	-15.68	1.97
	$V_r^{\neq}$	23.33	20.16	24.00	19.43	18.40	17.63	19.11	20.14	18.84	35.65
$F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$	$V_f^{\neq}$	2.80	1.26	2.35	1.11	0.33	0.50	1.24	1.93	-0.09	15.60
	$V_r^{\neq}$	31.69	28.02	32.58	27.71	27.12	26.65	27.85	28.76	27.06	41.91
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	$V_f^{\neq}$	-1.82	-3.86	-1.51	-4.82	-5.59	-6.13	-5.15	-6.23	-5.94	-2.96
	$V_r^{\neq}$	20.49	17.22	20.04	16.68	15.16	14.71	16.32	14.29	14.54	17.99
$OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$	$V_f^{\neq}$	11.42	8.56	12.30	8.32	7.97	7.77	8.52	7.61	7.37	7.73
	$V_r^{\neq}$	51.82	47.42	50.26	48.23	46.26	45.94	48.59	45.40	45.05	46.57
Unimolecular and Association Reactions											
$H + N_2 \rightarrow HN_2$	$V_f^{\neq}$	11.06	12.58	11.40	9.13	10.68	11.57	8.89	7.84	7.82	7.10
	$V_r^{\neq}$	13.69	13.05	13.69	11.92	12.76	12.60	11.79	11.06	10.96	11.49
$H + CO \rightarrow HCO$	$V_f^{\neq}$	1.63	4.07	1.50	0.55	2.40	3.11	0.33	-0.61	-0.56	-0.73
	$V_r^{\neq}$	26.11	26.67	24.90	25.67	25.60	25.47	25.57	24.60	24.65	26.04
$H + C_2H_4 \rightarrow CH_3CH_2$	$V_f^{\neq}$	1.21	4.36	0.62	0.97	2.55	3.35	0.81	-0.19	-0.07	0.37
	$V_r^{\neq}$	46.97	44.31	45.51	44.54	43.79	43.33	44.27	41.90	41.87	43.29
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	$V_f^{\neq}$	5.93	4.74	7.89	4.98	4.10	3.47	4.15	5.62	6.06	7.47
	$V_r^{\neq}$	36.70	31.70	33.73	33.87	30.74	30.98	34.40	29.80	29.40	31.26
$HCN \rightarrow HNC$	$V_f^{\neq}$	47.48	47.19	48.29	47.07	46.50	46.40	46.75	47.66	47.70	46.77
	$V_r^{\neq}$	34.65	33.37	35.95	33.33	33.58	33.20	33.03	33.88	33.79	32.58

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

[b] The MG3S basis set and QCISD/MG3 geometries are used for all calculations in this table.

Table S4: Barrier Heights Calculated by Hybrid Meta DFT Methods[a,b]

Reactions		BB1K	MPWB1K	MPWKCIS1K	B1B95	MPW1B95	MPW1KCIS	TPSS1KCIS	TPSSh
Heavy-atom transfer reactions									
$H + N_2O \rightarrow OH + N_2$	$V_f^{\neq}$	17.99	17.80	16.69	16.00	15.86	12.82	12.86	9.85
	$V_r^{\neq}$	80.79	80.80	84.70	72.78	73.21	69.07	68.31	66.31
$H + FH \rightarrow HF + H$	$V_f^{\neq}$	40.50	40.48	39.36	36.98	37.12	32.60	32.35	29.81
	$V_r^{\neq}$	40.50	40.48	39.36	36.98	37.12	32.60	32.35	29.81
$H + ClH \rightarrow HCl + H$	$V_f^{\neq}$	18.18	18.10	17.24	16.33	16.34	13.66	13.32	9.48
	$V_r^{\neq}$	18.18	18.10	17.24	16.33	16.34	13.66	13.32	9.48
$H + FCH_3 \rightarrow HF + CH_3$	$V_f^{\neq}$	31.57	31.66	29.64	27.76	28.04	22.40	22.49	20.04
	$V_r^{\neq}$	55.22	54.80	57.23	51.00	50.69	48.90	46.91	45.63
$H + F_2 \rightarrow HF + F$	$V_f^{\neq}$	-1.10	-1.34	-2.75	-2.96	-3.02	-6.59	-6.51	-8.76
	$V_r^{\neq}$	108.88	109.02	110.64	100.38	101.09	94.11	92.13	90.14
$CH_3 + FCl \rightarrow CH_3F + Cl$	$V_f^{\neq}$	4.95	4.63	5.32	1.46	1.26	-1.52	-2.24	-2.51
	$V_r^{\neq}$	62.13	62.22	62.10	56.15	56.57	50.58	49.52	48.67
Nucleophilic substitution reactions									
$F^- + CH_3F \rightarrow FCH_3 + F^-$	$V_f^{\neq}$	0.86	0.29	0.61	-1.27	-1.83	-4.01	-5.72	-6.60
	$V_r^{\neq}$	0.86	0.29	0.61	-1.27	-1.83	-4.01	-5.72	-6.60
$F^-\cdots CH_3F \rightarrow FCH_3 \cdots F^-$	$V_f^{\neq}$	14.43	14.58	14.04	12.18	12.51	9.64	8.52	7.71
	$V_r^{\neq}$	14.43	14.58	14.04	12.18	12.51	9.64	8.52	7.71
$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	$V_f^{\neq}$	3.95	3.55	3.51	2.12	1.75	-0.38	-1.90	-3.09
	$V_r^{\neq}$	3.95	3.55	3.51	2.12	1.75	-0.38	-1.90	-3.09
$Cl^-\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$	$V_f^{\neq}$	13.45	13.63	13.03	11.47	11.82	9.20	8.12	7.07
	$V_r^{\neq}$	13.45	13.63	13.03	11.47	11.82	9.20	8.12	7.07

$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	$V_f^{\neq}$	-12.77	-13.35	-13.10	-14.08	-14.70	-16.17	-18.07	-19.30
	$V_r^{\neq}$	23.44	23.07	23.19	20.56	20.30	17.21	16.69	16.17
$F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$	$V_f^{\neq}$	3.02	3.13	2.61	1.81	4.97	0.27	-1.43	-2.03
	$V_r^{\neq}$	31.77	32.00	31.49	28.67	29.16	25.40	25.20	24.66
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	$V_f^{\neq}$	-1.38	-1.95	-1.66	-3.49	-4.08	-6.28	-7.75	-8.59
	$V_r^{\neq}$	20.37	19.91	20.25	17.61	17.20	14.46	12.30	11.17
$OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$	$V_f^{\neq}$	11.88	12.07	11.47	9.48	9.86	6.75	5.77	4.91
	$V_r^{\neq}$	50.30	50.65	50.34	47.47	48.06	44.92	43.38	42.60
Unimolecular and Association Reactions									
$H + N_2 \rightarrow HN_2$	$V_f^{\neq}$	12.60	12.50	11.22	11.02	11.00	8.16	7.93	4.46
	$V_r^{\neq}$	13.01	13.23	13.58	11.58	11.92	10.93	10.54	9.57
$H + CO \rightarrow HCO$	$V_f^{\neq}$	2.56	2.40	1.59	1.72	1.59	-0.14	-0.51	-4.20
	$V_r^{\neq}$	24.87	24.95	25.89	24.54	24.66	25.21	25.25	24.15
$H + C_2H_4 \rightarrow CH_3CH_2$	$V_f^{\neq}$	2.13	1.90	1.15	1.86	1.61	0.59	0.16	-3.82
	$V_r^{\neq}$	44.01	44.19	46.50	42.04	42.36	42.78	42.84	41.54
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	$V_f^{\neq}$	6.34	5.68	7.29	5.56	4.83	5.56	4.72	4.16
	$V_r^{\neq}$	34.66	35.09	34.66	32.21	32.87	30.23	30.06	29.83
$HCN \rightarrow HNC$	$V_f^{\neq}$	46.80	46.83	48.06	46.48	46.54	47.42	47.88	47.77
	$V_r^{\neq}$	34.09	34.25	34.99	33.04	33.28	33.01	33.04	32.97

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

[b] The MG3S basis set and QCISD/MG3 geometries are used for all calculations in this table.

Table S5: Barrier Heights Calculated by Ab Initio WFT Methods[a,b]

Reactions		QCISD(T)	QCISD	MP4SDQ	MP2	MP3	HF
Heavy-atom transfer reactions							
$H + N_2O \rightarrow OH + N_2$	$V_f^{\neq}$	19.09	19.89	26.63	37.24	26.73	28.28
	$V_r^{\neq}$	83.06	90.33	95.90	89.08	100.04	123.72
$H + FH \rightarrow HF + H$	$V_f^{\neq}$	44.15	45.29	46.56	48.35	47.83	58.58
	$V_r^{\neq}$	44.15	45.29	46.56	48.35	47.83	58.58
$H + ClH \rightarrow HCl + H$	$V_f^{\neq}$	20.04	21.03	22.48	24.66	23.59	32.09
	$V_r^{\neq}$	20.04	21.03	22.48	24.66	23.59	32.09
$H + FCH_3 \rightarrow HF + CH_3$	$V_f^{\neq}$	32.00	33.45	35.47	37.31	37.21	47.55
	$V_r^{\neq}$	57.67	60.29	61.95	60.36	63.89	73.72
$H + F_2 \rightarrow HF + F$	$V_f^{\neq}$	2.58	2.98	17.58	29.31	20.15	-9.85
	$V_r^{\neq}$	106.49	111.43	125.40	131.99	130.00	123.95
$CH_3 + FCl \rightarrow CH_3F + Cl$	$V_f^{\neq}$	6.55	9.20	15.28	19.36	16.97	15.38
	$V_r^{\neq}$	62.66	66.89	72.87	76.48	75.24	80.16
Nucleophilic substitution reactions							
$F^- + CH_3F \rightarrow FCH_3 + F^-$	$V_f^{\neq}$	-1.66	0.35	0.39	-0.15	3.33	7.69
	$V_r^{\neq}$	-1.66	0.35	0.39	-0.15	3.33	7.69
$F^{-}\cdots CH_3F \rightarrow FCH_3 \cdots F^-$	$V_f^{\neq}$	12.90	14.55	14.51	13.89	17.38	20.05
	$V_r^{\neq}$	12.90	14.55	14.51	13.89	17.38	20.05
$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	$V_f^{\neq}$	2.14	4.26	4.77	3.99	5.33	7.78
	$V_r^{\neq}$	2.14	4.26	4.77	3.99	5.33	7.78
$Cl^{-}\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$	$V_f^{\neq}$	12.78	14.45	14.95	14.63	15.68	16.38
	$V_r^{\neq}$	12.78	14.45	14.95	14.63	15.68	16.38

F- + $CH_3Cl \rightarrow FCH_3 + Cl$-	$V_f^{\neq}$	-14.75	-13.03	-12.68	-12.11	-11.84	-10.73
	$V_r^{\neq}$	21.87	23.92	23.85	21.81	27.40	33.65
F-···$CH_3Cl \rightarrow FCH_3$···Cl-	$V_f^{\neq}$	2.04	3.15	3.39	3.81	4.29	3.95
	$V_r^{\neq}$	31.28	33.04	32.99	31.26	36.51	40.97
OH- + $CH_3F \rightarrow HOCH_3$ + F-	$V_f^{\neq}$	-4.16	-1.81	-1.72	-2.82	0.76	6.63
	$V_r^{\neq}$	16.02	18.73	18.77	17.54	21.98	28.24
OH-···$CH_3F \rightarrow HOCH_3$···F-	$V_f^{\neq}$	10.22	12.21	12.25	11.29	14.78	18.77
	$V_r^{\neq}$	47.45	49.01	48.92	48.63	52.98	53.67
Unimolecular and Association Reactions							
H + $N_2 \rightarrow HN_2$	$V_f^{\neq}$	15.78	16.07	20.82	28.83	22.21	23.20
	$V_r^{\neq}$	10.70	11.49	11.06	8.06	12.72	13.73
H + CO $\rightarrow$ HCO	$V_f^{\neq}$	4.06	4.48	5.33	6.33	5.82	9.10
	$V_r^{\neq}$	21.97	22.50	22.52	21.72	23.32	17.48
H + $C_2H_4 \rightarrow CH_3CH_2$	$V_f^{\neq}$	2.88	3.00	6.46	9.88	7.74	4.19
	$V_r^{\neq}$	41.92	43.86	47.19	45.97	48.14	44.22
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	$V_f^{\neq}$	6.97	8.21	11.67	13.37	12.79	12.09
	$V_r^{\neq}$	32.56	33.86	37.54	40.67	39.26	32.86
HCN $\rightarrow$ HNC	$V_f^{\neq}$	48.44	48.62	49.35	52.93	49.55	47.88
	$V_r^{\neq}$	33.52	34.12	34.71	35.19	35.63	38.07

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

[b] The MG3S basis set and QCISD/MG3 geometries are used for all calculations in this table.

Table S6: AE6 Database

Molecule	D_e (kcal/mol)
propyne (C_3H_4)	704.79
glyoxal ($C_2H_2O_2$)	633.35
cyclobutane (C_4H_8)	1149.01
SiH_4	322.40
SiO	192.08
S_2	101.67

Table S7: Barrier Heights and Energies of Reaction (kcal/mol) for the Kinetics9 database[a]

Reaction	Best Estimates		
	$V_f^{\neq}$	$V_r^{\neq}$	ΔE
$OH + CH_4 \rightarrow CH_3 + H_2O$	6.7	19.6	-12.9
$H + OH \rightarrow O + H_2$	10.7	13.1	-2.4
$H + H_2S \rightarrow H_2 + HS$	3.5	17.3	-13.7

[a] from Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 8996; **2004**; *108;* 1460 (E).