Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPLEMENTARY INFORMATION

Rethinking the $X^- + CH_3Y$ [X = OH, SH, CN, NH_2, PH_2; Y = F, Cl, Br, I] S_N2 reactions

Domonkos A. Tasi, Zita Fábián, and Gábor Czakó*

Interdisciplinary Excellence Centre and Department of Physical Chemistry and Materials Science, Institute of Chemistry, University of Szeged, Rerrich Béla tér 1, Szeged H-6720, Hungary

* gczako@chem.u-szeged.hu

Content

Relative energies for the stationary points of the potential energy surfaces of the $X^- + CH_3Y$ [X = OH, SH, CN, NH_2, PH_2; Y = F, Cl, Br, I] S_N2 reactions obtained at different levels of theory

Table S1. Benchmark classical and adiabatic energies (kcal/mol) of the stationary points relative to the reactants for the $OH^- + CH_3Y$ [Y = F, Cl, Br, I] S_N2 reactions (data are taken from D. A. Tasi, Z. Fábián and G. Czakó, *J. Phys. Chem. A*, 2018, **122**, 5773)

OH^-+CH_3F	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
PreMIN	−14.08	−13.87	−13.87	−13.74	0.60	−13.14
WaldenTS	−4.52	−2.44	−2.71	−2.59	0.81	−1.78
PostHMIN	−50.40	−50.32	−50.19	−50.05	1.75	−48.31
FSTS	40.04	42.56	42.44	42.74	0.36	43.10
DITS	19.71	17.00	17.23	17.45	−0.55	16.89
F^-+CH_3OH	−21.13	−19.76	−19.82	−19.95	2.19	−17.76
OH^-+CH_3Cl	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
HMIN	−16.40	−16.39	−16.33	−16.20	0.55	−15.65
HTS	−15.75	−15.47	−15.64	−15.55	0.58[g]	−14.97
PreMIN	−15.83	−15.49	−15.71	−15.62	0.61[g]	−15.01
WaldenTS	−13.41	−12.83	−13.26	−13.21	0.62	−12.59
PostHMIN	−67.97	−68.77	−68.91	−69.04	3.68[g]	−65.36
FSMIN	−1.12	−2.74	−2.38	−2.24	0.43	−1.81
FSTS	28.73	28.92	28.64	28.81	0.39	29.19
DITS	6.66	3.31	3.51	3.60	−0.13	3.48
Cl^-+CH_3OH	−51.68	−52.10	−52.37	−52.65	3.17	−49.48
OH^-+CH_3Br	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
HMIN	−17.13	−17.54	−17.33	−17.17	0.48	−16.70
HTS	−16.06	−16.30	−16.28	−16.17	0.57	−15.60
PreMIN	−16.18	−16.53	−16.53	−16.41	0.50	−15.92
WaldenTS	−15.50	−16.24	−16.33	−16.24	0.39[g]	−15.84
PostHMIN	−72.11	−74.98	−74.75	−74.95	4.12	−70.83
FSMIN	−10.29	−11.37	−11.33	−11.21	0.55	−10.66
FSTS	23.70	22.51	22.30	22.44	0.44	22.88
DITS	3.90	0.63	0.89	1.01	0.01	1.01
Br^-+CH_3OH	−57.80	−60.59	−60.41	−60.80	3.58	−57.23
OH^-+CH_3I	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
HMIN	−18.40	−18.89	−18.64	−18.48	0.42	−18.06
HTS	−16.40	−16.74	−16.69	−16.57	0.50	−16.07
PostHMIN	−76.27	−79.30	−79.08	−79.43	4.49	−74.94
FSMIN	−22.90	−24.09	−24.10	−24.05	0.68	−23.37
FSTS	18.41	17.19	17.03	17.10	0.58	17.67
DITS	−0.55	−4.20	−4.13	−4.05	0.18	−3.87
I^-+CH_3OH	−64.18	−67.16	−67.08	−67.71	3.98	−63.74

[a] MP2/aug-cc-pVDZ

[b] CCSD(T)-F12b/aug-cc-pVDZ

[c] CCSD(T)-F12b/aug-cc-pVTZ

[d] CCSD(T)-F12b/aug-cc-pVQZ

[e] ΔZPE(CCSD(T)-F12b/aug-cc-pVTZ)

[f] QZ + ΔZPE

[g] These ΔZPE values differ from those of *J. Phys. Chem. A*, 2018, **122**, 5773, because here ZPEs are computed using all the real harmonic frequencies, whereas in the previous work the low frequencies (< 50 cm^{-1}) were not considered during the ZPE calculations.

Table S2. Benchmark classical and adiabatic energies (kcal/mol) of the stationary points relative to the reactants for the $SH^- + CH_3Y$ [Y = F, Cl, Br, I] S_N2 reactions

SH^-+CH_3F	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
PreMIN	−9.53	−9.05	−8.92	−8.88	0.32	−8.56
WaldenTS	10.91	13.97	13.73	13.84	−0.10	13.74
PostHMIN	−29.75	−28.10	−27.90	−27.76	1.43	−26.33
PostHMIN2	−7.34	−5.20	−4.76	−4.56	0.50	−4.07
FSTS	50.75	53.23	53.10	53.41	−0.49	52.92
DITS	55.09	55.05	55.55	55.82	−3.93	51.89
F^-+CH_3SH	7.50	10.45	10.72	10.71	0.41	11.12
SH^-+CH_3Cl	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
PreMIN	−10.74	−10.09	−10.11	−10.12	0.25	−9.86
WaldenTS	−2.74	−1.06	−1.48	−1.53	0.17	−1.36
PostHMIN	−36.42	−34.77	−34.50	−34.57	1.54	−33.03
PostHMIN2	−31.29	−30.11	−29.88	−29.94	1.68	−28.26
WaldenPostMIN	−31.16	−29.96	−29.72	−29.85	1.44	−28.41
FSMIN	1.17	0.56	0.83	0.86	0.15	1.02
FSTS	40.45	40.39	40.19	40.29	−0.62	39.67
DITS	43.56	43.14	43.60	43.76	−3.34	40.42
Cl^-+CH_3SH	−23.05	−21.89	−21.84	−22.00	1.39	−20.61
SH^-+CH_3Br	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
PreMIN	−11.11	−10.84	−10.69	−10.69	0.25	−10.43
WaldenTS	−6.14	−6.04	−6.15	−6.20	0.24	−5.95
PostHMIN	−40.98	−41.47	−40.85	−41.01	1.98	−39.03
PostHMIN2	−36.48	−37.46	−36.85	−37.02	2.04	−34.98
WaldenPostMIN	−36.65	−37.62	−37.02	−37.26	1.85	−35.41
FSMIN	−3.55	−3.54	−3.56	−3.55	0.22	−3.33
FSTS	35.75	34.15	34.05	34.10	−0.43	33.67
DITS	41.08	40.76	41.30	41.47	−3.27	38.20
Br^-+CH_3SH	−29.16	−30.38	−29.87	−30.15	1.80	−28.35
SH^-+CH_3I	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
HMIN	−10.64	−10.35	−10.13	−10.07	0.37	−9.70
PreMIN	−11.51	−11.19	−11.02	−11.03	0.28	−10.75
WaldenTS	−8.97	−8.76	−8.76	−8.85	0.34	−8.51
PostHMIN	−45.60	−46.35	−45.76	−46.10	2.43	−43.67
PostHMIN2	−41.75	−42.96	−	−42.86	2.27	−40.58
WaldenPostMIN	−42.20	−43.35	−42.83	−43.29	2.27	−41.02
FSMIN	−10.54	−10.48	−10.71	−10.81	0.22	−10.59
FSTS	31.55	29.86	29.72	29.67	−0.56	29.11
DITS	37.33	36.67	37.07	37.20	−3.07	34.12
I^-+CH_3SH	−35.54	−36.96	−36.54	−37.06	2.20	−34.86

[a] MP2/aug-cc-pVDZ

[b] CCSD(T)-F12b/aug-cc-pVDZ

[c] CCSD(T)-F12b/aug-cc-pVTZ

[d] CCSD(T)-F12b/aug-cc-pVQZ

[e] ΔZPE(CCSD(T)-F12b/aug-cc-pVTZ)

[f] QZ + ΔZPE

Table S3. Benchmark classical and adiabatic energies (kcal/mol) of the stationary points relative to the reactants for the $CN^- + CH_3Y$ [Y = F, Cl, Br, I] S_N2 reactions

CN^-+CH_3F	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
HMIN2	−10.12	−9.50	−9.45	−9.39	0.45	−8.95
PreMIN	−9.51	−8.99	−8.97	−8.88	0.43	−8.46
WaldenTS	9.12	12.71	12.20	12.18	0.17	12.35
PostHMIN2	−31.01	−25.12	−25.66	−25.72	0.11	−25.61
FSTS	53.43	56.56	56.08	56.19	−0.51	55.68
DITS	51.12	52.43	52.26	52.38	−3.16	49.21
F^-+CH_3CN	−7.28	−0.32	−1.12	−1.44	0.63	−0.81
CN^-+CH_3Cl	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
HMIN2	−11.18	−10.34	−10.47	−10.46	0.34	−10.11
PreMIN	−10.34	−9.64	−9.80	−9.75	0.32	−9.43
WaldenTS	−1.42	0.66	−0.05	−0.18	0.35	0.18
WaldenPostMIN	−51.94	−47.06	−47.85	−48.25	1.67	−46.58
PostHMIN2	−52.20	−47.26	−48.09	−48.44	1.80	−46.65
FSMIN	1.01	0.54	0.72	0.80	0.28	1.08
FSTS	47.12	47.76	47.11	47.04	−0.56	46.48
DITS	37.84	38.72	38.47	38.45	−2.39	36.06
Cl^-+CH_3CN	−37.83	−32.65	−33.67	−34.15	1.61	−32.53
CN^-+CH_3Br	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
HMIN1	−9.59	−9.38	−9.28	−9.22	0.36	−8.86
HMIN2	−11.30	−10.86	−10.79	−10.77	0.34	−10.43
PreMIN	−10.48	−10.21	−10.14	−10.09	0.32	−9.77
WaldenTS	−4.16	−3.73	−4.04	−4.17	0.43	−3.74
WaldenPostMIN	−57.05	−54.30	−54.72	−55.22	2.07	−53.16
PostHMIN2	−57.03	−54.22	−54.64	−55.10	2.15	−52.95
FSMIN	−3.44	−3.50	−3.48	−3.39	0.34	−3.06
FSTS	43.29	42.23	41.79	41.67	−0.39	41.28
DITS	35.34	36.45	36.30	36.30	−2.30	34.00
Br^-+CH_3CN	−43.95	−41.14	−41.71	−42.30	2.02	−40.28
CN^-+CH_3I	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
HMIN1	−10.06	−9.82	−9.65	−9.57	0.52	−9.06
HMIN2	−11.34	−10.90	−10.82	−10.80	0.37	−10.43
HTS2	−9.99	−9.66	−9.58	−9.54	0.40	−9.14
PreMIN	−10.50	−10.23	−10.13	−10.09	0.29	−9.79
WaldenTS	−6.21	−5.77	−5.91	−6.07	0.46	−5.61
WaldenPostMIN	−62.10	−59.53	−59.99	−60.72	2.47	−58.25
PostHMIN2	−61.86	–	–	−61.12	2.40	−58.73
FSMIN	−10.35	−10.15	−10.15	−10.13	0.30	−9.83
FSTS	40.43	38.95	38.55	38.35	−0.31	38.04
DITS	31.51	32.26	31.97	31.92	−2.04	29.88
I^-+CH_3CN	−50.32	−47.72	−48.38	−49.21	2.42	−46.79

[a] MP2/aug-cc-pVDZ

[b] CCSD(T)-F12b/aug-cc-pVDZ

[c] CCSD(T)-F12b/aug-cc-pVTZ

[d] CCSD(T)-F12b/aug-cc-pVQZ

[e] ΔZPE(CCSD(T)-F12b/aug-cc-pVTZ)

[f] QZ + ΔZPE

Table S4. Benchmark classical and adiabatic energies (kcal/mol) of the stationary points relative to the reactants for the NH_2^- + CH_3Y [Y = F, Cl, Br, I] S_N2 reactions

$NH_2^-+CH_3F$	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
PreMIN	−13.13	−12.68	−12.55	−12.41	0.66	−11.75
WaldenTS	−5.56	−3.09	−3.21	−3.03	1.14	−1.89
PostHMIN	−59.41	−56.69	−56.53	−56.45	4.05	−52.40
FSTS	29.68	32.44	32.44	32.78	0.57	33.35
DITS	11.55	9.79	10.01	10.14	0.55	10.69
$F^-+CH_3NH_2$	−41.65	−38.09	−38.15	−38.32	3.87	−34.46
$NH_2^-+CH_3Cl$	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
HMIN	−15.11	−14.68	−14.57	−14.44	0.77	−13.67
PreMIN	−14.88	−14.22	−14.30	−14.20	0.58	−13.62
WaldenTS	−13.66	−12.64	−12.92	−12.82	0.68	−12.14
PostHMIN	−82.37	−80.73	−80.81	−81.01	5.33	−75.69
FSMIN	−1.03	−2.21	−1.88	−1.70	0.58	−1.12
FSTS	20.63	18.86	19.31	19.56	0.37	19.93
DITS	−1.53	−3.83	−3.63	−3.59	0.99	−2.60
$Cl^-+CH_3NH_2$	−72.20	−70.43	−70.70	−71.03	4.85	−66.18
$NH_2^-+CH_3Br$	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
HMIN	−15.77	−15.70	−15.44	−15.29	0.79	−14.50
PreMIN	−15.46	–	–	−14.27	0.58	−13.70
PostHMIN	−87.39	−87.87	−87.58	−87.87	5.67	−82.21
FSMIN	−12.83	−12.89	−12.64	−12.52	0.99	−11.52
FSTS	16.13	12.56	13.26	13.50	−0.17	13.32
DITS	−4.42	−6.63	−6.36	−6.29	1.10	−5.19
$Br^-+CH_3NH_2$	−78.31	−78.92	−78.74	−79.18	5.26	−73.92
$NH_2^-+CH_3I$	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
HMIN	−16.85	−16.80	−16.50	−16.34	0.68	−15.66
PreTS	−15.95	−15.85	−15.71	−15.62	0.40	−15.22
PostHMIN	−92.51	−93.17	−92.91	−93.40	6.02	−87.38
FSMIN	−25.96	−26.08	−25.85	−25.78	1.33	−24.45
FSTS	12.20	7.81	8.81	9.03	−0.39	8.64
DITS	−9.15	−11.79	−11.72	−11.70	1.37	−10.33
$I^-+CH_3NH_2$	−84.69	−85.50	−85.41	−86.09	5.66	−80.43

[a] MP2/aug-cc-pVDZ

[b] CCSD(T)-F12b/aug-cc-pVDZ

[c] CCSD(T)-F12b/aug-cc-pVTZ

[d] CCSD(T)-F12b/aug-cc-pVQZ

[e] ΔZPE(CCSD(T)-F12b/aug-cc-pVTZ)

[f] QZ + ΔZPE

Table S5. Benchmark classical and adiabatic energies (kcal/mol) of the stationary points relative to the reactants for the PH_2^- + CH_3Y [Y = F, Cl, Br, I] S_N2 reactions

PH_2^-+CH_3F	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
PreMIN	−8.68	−8.13	−8.02	−7.98	0.46	−7.52
WaldenTS	6.31	9.95	9.72	9.75	0.09	9.84
PostHMIN	−35.28	−32.92	−32.87	−32.79	1.58	−31.21
PostHMIN2	−28.81	−25.75	−25.51	−25.51	1.32	−24.19
FSTS	41.98	45.41	44.91	45.10	−0.66	44.44
DITS	48.67	48.55	49.06	49.16	−3.10	46.06
F^-+CH_3PH_2	−15.47	−11.52	−11.44	−11.67	1.34	−10.34
PH_2^-+CH_3Cl	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
PreTS	−9.65	−8.91	−8.96	−8.95	0.30	−8.65
PreMIN	−9.84	−9.08	−9.16	−9.16	0.14	−9.02
WaldenTS	−5.80	−3.90	−4.21	−4.30	0.20	−4.11
PostHMIN2	−53.91	−51.80	−51.75	−52.03	2.42	−49.62
FSMIN	1.22	0.85	1.09	1.12	0.23	1.35
FSTS	32.76	31.44	31.93	31.99	−0.39	31.60
DITS	36.04	35.16	35.67	35.66	−2.36	33.30
Cl^-+ CH_3PH_2	−46.03	−43.85	−44.00	−44.38	2.32	−42.06
PH_2^-+CH_3Br	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
PreTS	−9.82	−9.41	−9.28	−9.27	0.29	−8.98
PreMIN	−10.51	−10.16	−10.02	−10.03	0.27	−9.76
WaldenTS	−9.19	−8.70	−8.68	−8.75	0.20	−8.55
WaldenPostMIN	−57.47	−57.66	−57.29	−57.74	2.63	−55.11
PostHMIN2	−59.27	−59.29	−58.89	−59.27	2.75	−56.53
FSMIN	−4.78	−4.38	−4.41	−4.43	0.27	−4.16
FSTS	27.73	−	−	29.52	0.25	29.77
DITS	33.53	32.86	33.38	33.39	−2.18	31.21
Br^-+ CH_3PH_2	−52.14	−52.35	−52.03	−52.53	2.72	−49.81
PH_2^-+CH_3I	MP2[a]	DZ[b]	TZ[c]	QZ[d]	ΔZPE[e]	Adiabatic[f]
PreTS	−9.95	−9.51	−9.36	−9.36	0.35	−9.01
PostHMIN2	−64.72	−64.90	−64.58	−65.17	3.22	−61.95
FSMIN	−14.32	−13.51	−13.66	−13.84	0.38	−13.46
FSTS	23.53	−	−	25.37	0.43	25.81
DITS	29.50	28.28	28.60	28.56	−2.06	26.50
I^-+ CH_3PH_2	−58.52	−58.92	−58.71	−59.44	3.12	−56.32

[a] MP2/aug-cc-pVDZ

[b] CCSD(T)-F12b/aug-cc-pVDZ

[c] CCSD(T)-F12b/aug-cc-pVTZ

[d] CCSD(T)-F12b/aug-cc-pVQZ

[e] ΔZPE(CCSD(T)-F12b/aug-cc-pVTZ)

[f] QZ + ΔZPE