Supplementary Material for PCCP

Electronic Supplementary Information for "Ab initio study of a S_N2 reaction of methyl *p*-nitrobenzenesulfonate and chloride anion in [mmim][PF_6]"

November 17, 2009

The Electronic Supplementary Information includes the following data;
(1) Cartesian coordinate of the reactant, TS, and product.
(2) Potential energy obtained by RHF and CCSD level calculations.
(3) Selected bond lengths and the reaction coordinate in the optimized structures in gas phase and in solutions.
(4) Activation free energy evaluated with the solvation free energy in different forms.

Table 1: Cartesian coordinate of methyl *p*-nitrobenzenesulfonate (*p*-NBS). All units are in angstrom.

atom	X	Y	Z
C	0.1950865680	-0.4170522423	0.0000000000
C	0.1454978158	0.2535234917	-1.2115320612
C	0.1454978158	0.2535234917	1.2115320612
C	0.0323553797	1.6334247530	-1.2141722194
C	0.0323553797	1.6334247530	1.2141722194
C	-0.0250240392	2.2927104509	0.0000000000
H	0.2060351678	-0.2899308168	-2.1344545114
H	0.2060351678	-0.2899308168	2.1344545114
H	-0.0064967765	2.1842189842	-2.1318565342
H	-0.0064967765	2.1842189842	2.1318565342
N	-0.1450757996	3.7540337619	0.0000000000
O	-0.1908678355	4.3018120204	-1.0585717143
O	-0.1908678355	4.3018120204	1.0585717143
S	0.3307975055	-2.1794892178	0.0000000000
O	0.9032421189	-2.6121439636	-1.2316188087
O	0.9032421189	-2.6121439636	1.2316188087
O	-1.2005474280	-2.5362105490	0.0000000000
C	-1.5670840237	-3.9253578174	0.0000000000
H	-2.6440188696	-3.9271892134	0.0000000000
H	-1.1866363269	-4.4033235553	-0.8902971989
H	-1.1866363269	-4.4033235553	0.8902971989

Table 2: Cartesian coordinate of TS. All units are in angstrom.

atom	X	Y	Z
C	0.1982525034	-0.6838693987	0.0000000000
C	0.1141742484	-0.0043307690	-1.2060626339
C	0.1141742484	-0.0043307690	1.2060626339
C	-0.0618310195	1.3685097782	-1.2123604817
C	-0.0618310195	1.3685097782	1.2123604817
C	-0.1487983593	2.0310300609	0.0000000000
H	0.1980556350	-0.5470367424	-2.1276277038
H	0.1980556350	-0.5470367424	2.1276277038
H	-0.1272520570	1.9137829625	-2.1321107840
H	-0.1272520570	1.9137829625	2.1321107840
N	-0.3310233285	3.4798728631	0.0000000000
O	-0.4009481418	4.0353120698	-1.0567869452
O	-0.4009481418	4.0353120698	1.0567869452
S	0.3869468794	-2.4618768519	0.0000000000
O	1.0631693660	-2.7952113355	-1.2259805237
O	1.0631693660	-2.7952113355	1.2259805237
O	-1.0308212693	-2.9164576124	0.0000000000
C	-1.5688057250	-4.7389826154	0.0000000000
H	-2.5851033603	-4.4322266348	0.0000000000
H	-1.0952004021	-4.9847761306	-0.9199992683
H	-1.0952004021	-4.9847761306	0.9199992683
Cl	-2.4842189599	-7.0614491850	0.0000000000

Table 3: Cartesian coordinate of *p*-NBS anion. All units are in angstrom.

atom	X	Y	Z
C	0.2110280581	-0.7024692012	0.0000000000
C	0.1201654099	-0.0137270348	-1.2030935878
C	0.1201654099	-0.0137270348	1.2030935878
C	-0.0713771767	1.3562273597	-1.2114853574
C	-0.0713771767	1.3562273597	1.2114853574
C	-0.1683500251	2.0224462803	0.0000000000
H	0.2114131234	-0.5560477466	-2.1243204846
H	0.2114131234	-0.5560477466	2.1243204846
H	-0.1423506660	1.8994956159	-2.1323961708
H	-0.1423506660	1.8994956159	2.1323961708
N	-0.3714939961	3.4635905355	0.0000000000
O	-0.4509757590	4.0237014167	-1.0560279812
O	-0.4509757590	4.0237014167	1.0560279812
S	0.3870760080	-2.4981128104	0.0000000000
O	1.1157125497	-2.7789715940	-1.2211798349
O	1.1157125497	-2.7789715940	1.2211798349
O	-0.9832540660	-2.9717405409	0.0000000000

Table 4: Cartesian coordinate of methyl cloride. All units are in angstrom.

atom	X	Y	Z
Cl	0.0000000000	0.0000000000	-0.3113498333
C	0.0000000000	0.0000000000	-2.0971904468
H	-0.5113291425	0.8856480543	-2.4377142400
H	-0.5113291425	-0.8856480543	-2.4377142400
H	1.0226582851	0.0000000000	-2.4377142400

Table 5: Potential energy obtained by RHF and CCSD level calculations.

	species	*E*(RHF) / a.u.	*E*(CCSD) / a.u.
reactant	*p*-NBS	-1095.2345799032	-1097.3769562663
	chloride anion	-459.5396608917	-459.6834655691
TS		-1554.7802741306	-1557.0787006984
product	*p*-NBS anion	-1055.7152053475	-1057.7267722172
	methyl chloride	-499.0941581388	-499.3856986061

Table 6: Selected bond lengths and the reaction coordinate in the optimized structures in gas phase and in solutions. All units are in angstrom.

R	comment	$r(O_{S1}–CH_3)$	$r(CH_3–Cl)$	relative energy[a] / kcal mol^{-1}
-0.596	optimized TS in gas	1.900	2.496	0.00
-0.469	optimized TS in DCM	1.949	2.418	0.00
-0.5	approximated TS in DCM[b]	1.955	2.455	0.18
-0.412	optimized TS in [mmim][PF_6]	2.003	2.415	0.00
-0.4	approximated TS in [mmim][PF_6][b]	2.005	2.405	0.58

[a] The energy difference between the optimized and approximated TSs. [b] The highest energy point in each solvent evaluated from the gas phase optimized structures.

Table 7: Activation free energy evaluated with the different free energy formulae. The values were computed based on the coupling with RHF level. All units are in kcal mol^{-1}.

free energy form	$\Delta\mathscr{A}^{\ddagger}$ ([mmim][PF_6])	$\Delta\mathscr{A}^{\ddagger}$ (DCM)	difference
KH (Kovalenko-Hirata)	22.52	12.59	9.93
HNC (hyper-netted chain)	24.26	13.98	10.28
GF (Gaussian Fluctuation)	27.40	19.74	7.66