Electronic Supplementary Information for PCCP

Supplementary Information

Theoretical investigation of the conformation, acidity, basicity and hydrogen bond ability of halogenated ethers

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TABLE 1S Selected NBO parameters in isolated halogenated ethers (σ* occupancies and s-orbital character at C carbon in CH bond). Results of MP2/6-311++G(d,p) calculations.

	I	**II**	**III**	**IV**	**V**
$\sigma^*(C_1H_6)$	0.008	0.021	0.020	0.037	0.035
$\sigma^*(C_3H_7)$		0.014	-	0.012	-
$\sigma^*(C_3H_9)$	0.008	0.007	0.020	0.007	0.036
$\%s\ C_1(H_4)$	25.92	27.38	27.88	-	-
$\%s\ C_1(H_6)$	25.64	27.02	27.08	27.76	28.89
$\%s\ C_3(H_7)$	25.92	25.99	-	26.66	-
$\%s\ C_3(H_9)$	25.64	25.81	27.08	25.79	30.08

TABLE 2S $E^{(2)}$ energies (kcal mol^{-1}) from lone pair of O to the σ* orbitals in the protonated ethers. The numbers in parentheses indicate the differences between the protonated and isolated molecules. Results of MP2/6-311++G(d,p) calculations.

	I(H^+)	**II(H^+)**	**III(H^+)**	**IV(H^+)**	**V(H^+)**
LP(1)O →					
$\sigma^*(C_1H_4)$	1.45(+0.47)	0.96(-2.66)	2.64(+1.03)	-	-
$\sigma^*(C_1H_6)$	0.91(-2.40)	1.41(-2.20)	0.59(-3.33)	1.24(-3.97)	0.00
$\sigma^*(C_3H_7)$	1.46(+0.48)	1.28(-0.90)	-	1.71(+0.95)	-
$\sigma^*(C_3H_8)$	3.27(+2.28)	3.01(+3.01)	0.99(-0.62)	2.89(+2.13)	-
$\sigma^*(C_3H_9)$	0.91(-2.40)	0.91(-2.08)	1.23(-2.58)	-	0.00
$\sigma^*(C_1X)$[a]	-	6.38(+5.72)	1.48(-0.80)	5.85(+1.42))	1.30 (-2.17)
$\sigma^*(C_3Cl_7)$	-	-	6.13(+3.85)	-	-
$\sigma^*(C_1F_5)$	-	-	-	-	5.63(+2.95)

[a] $X=Cl_5$ for II, III and IV, $X=Cl_4$ for V

Table 3S Selected NBO parameters in O-protonated halogenated ethers (σ* occupancies and and % s-character at C carbon in CH bond). Results of MP2/6-311++G(d,p) calculations.

	I(H^+)	**II(H^+)**	**III(H^+)**	**IV(H^+)**	**V(H^+)**
$\sigma^*(C_1H_4)$	0.004	0.021	0.022	-	-
$\sigma^*(C_1Cl_4)$	-	-	-	0.035	0.031
$\sigma^*(C_1Cl_5)$	-	0.015	0.008	0.043	0.051[a]
$\sigma^*(C_1H_6)$	0.003	0.019	0.019	0.040	0.036
$\sigma^*(C_3H_7)$	0.004	0.004	-	0.003	0.039[b]
$\sigma^*(C_3H_9)$	0.003	0.003	0.019	0.004	0.034
$\%sC_1(H_4)$	27.43	28.32	28.32	-	-
$\%sC_1(H_6)$	27.41	28.41	28.96	28.92	30.46
$\%sC_3(H_7)$	27.44	27.42	-	28.13	-
$\%sC_3(H_9)$	27.41	27.42	28.40	27.93	32.43

[a] Corresponds to $\sigma^*(C_1F_5)$. [b] Corresponds to $\sigma^*(C_3F_8)$.

TABLE 4S The NBO charges (e) on all the atoms in the isolated ethers. Results of MP2/6-311++G(d,p) calculations.

I		**II**		**III**		**IV**		**V**	
atom	charge	atom	charge	atom	charge	atom	charge	atom	charge
C_1	-0.095	C_1	0.103	C_1	0.078	C_1	0.206	C_1	0.614
O_2	-0.649	O_2	-0.636	O_2	-0.634	O_2	-0.640	O_2	-0.632
C_3	-0.095	C_3	-0.108	C_3	0.078	C_3	-0.120	C_3	0.995
H_4	0.131	H_4	0.145	H_4	0.170	Cl_4	-0.060	Cl_4	-0.064
H_5	0.131	Cl_5	-0.134	Cl_5	-0.110	Cl_5	-0.060	F_5	-0.408
H_6	0.158	H_6	0.172	H_6	0.179	H_6	0.183	H_6	0.163
H_7	0.131	H_7	0.137	Cl_7	-0.110	H_7	0.161	F_7	-0.393
H_8	0.131	H_8	0.157	H_8	0.170	H_8	0.161	F_8	-0.397
H_9	0.158	H_9	0.165	H_9	0.179	H_9	0.170	H_9	0.122

TABLE 5S $E^{(2)}$ energies (kcal mol^{-1}) from two lone pairs of O to the σ* orbitals in the isolated molecules. Results of B3LYP/6-311++G(d,p) calculations.

	I	**II**	**III**	**IV**	**V**
LP(1)O →					
σ*(C_1H_4)	0.78	3.14	1.50	-	-
σ*(C_1H_6)	2.49	2.75	2.98	3.81	3.21
σ*(C_3H_7)	0.78	1.65	-	0.57	-
σ*(C_3H_8)	0.78	0.00	1.50	0.57	-
σ*(C_3H_9)	2.49	2.31	2.98	2.50	2.92
σ*(C_1Cl_5)	-	0.58	1.87	3.99	2.83[a]
σ*(C_1F_5)	-	-	-	-	2.52
σ*(C_3F_7)	-	-	-	-	2.97
LP(2)O →					
σ*(C_1H_4)	6.51	3.88	4.72	-	-
σ*(C_1H_6)	0.00	0.64	0.00	0.00	0.00
σ*(C_3H_8)	6.51	6.07	4.72	4.79	-
σ*(C_1Cl_5)	-	21.95	15.50	16.49	13.72[b]
σ*(C_1F_5)	-	-	-	-	12.61
σ*(C_3F_7)	-	-	-	-	6.72

[a] $E^{(2)}$ from LP(1)O to σ*(C_1Cl_4). [b] $E^{(2)}$ from LP(2)O to σ*(C_1Cl_4).