Electronic Supplementary Information

Offsets between hyperconjugations, p→d donations and Pauli repulsions impact the bonding of E-O-E systems. Case study on elements of Group 14

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Oxonium Ions

Table S1. Equilibrium E-O-E angles and E-O bond distances within model $[(R_3E)_2OH]^+$ derivatives; computed NRT bond orders are displayed for the E-O bonds. Expected lengths for the E-O bonds are also presented (*i.e.* predicted values are obtained by summing the covalent radii of E and O atoms - *Cordero et. al., Dalton Trans. 2008, 21, 2832*).

Species	E	R	E-O-E (°)	E-O-H (°)	∑E-O-E + E-OH angles (°)	E-O (Å)	Σ*cov*(E+O) (Å)	NRT bond order (E-O)
$[(R_3E)_2OH]^+$	**C**	H	116.9	111.6	340.1	1.476	***1.42***	**1.02**
		Me	133.9	107.5	348.9	1.556		**0.91**
	Si	H	127.8	116.1	360.0	1.788	***1.77***	**1.03**
		Me	136.8	111.6	360.0	1.801		**1.00**
	Ge	H	130.0	115.0	358.8	1.914	***1.86***	**1.02**
		Me	136.8	111.6	360.0	1.940		**1.01**
	Sn	H	132.4	113.8	360.0	2.110	***2.05***	**1.03**
		Me	136.8	111.6	360.0	2.131		**1.02**

Discussions on the equilibrium structures of $[(R_3E)_2OH]^+$ oxonium cations

The calculated E-O-E angles and E-O bond lengths of model $[(R_3E)_2OH]^+$ oxonium cations (E = C, Si, Ge, Sn; R = H, Me) are presented in Table S1. Trends determined for these derivatives are in fact similar to those computed for the model $[(R_3E)_2OH]^+$ ions (for comparisons see also Table 1 in the Main Text, and the related discussions). Thus, the features of $[(R_3E)_2OH]^+$ cations can be summarized as follows: (i) the $[E_2OH]^+$ skeletons (E = Si, Ge, Sn) of inorganic cations are planar, in contrast to pyramidal $[C_2OH]^+$ moieties of organic counterparts; (ii) the E-O equilibrium distances of inorganic derivatives are equal (or slightly larger in some of the cases) than expected values obtained by summing the covalent radii of E and O atoms, while C-O bond distances of organic derivatives are larger than their reference length. Although the C-O bonds of the $[(t\text{-Bu})_2OH]^+$ molecule (*i.e.* their calculated distance are of 1.556 Å) are significantly larger than the 1.42 Å reference, they are at the same time with 0.041 Å shorter than analogue bond lengths of the $[(t\text{-Bu})_3O]^+$ species. These observations further emphasize the impact of the steric pressure, generated by the bulky *t*-Bu groups, on the C-O length of oxonium cations.

Table S2. Computed interaction-energies per E-O bond in case of attractions (*i.e.* ∑LP(O)→σ*(E-R) hyperconjugations, augmented by ∑LP(O)→d(E) donations in inorganic oxonium derivatives), and of Pauli repulsions (*i.e.* ∑LP(O)···σ(E-R) effects) occurring within model $[(R_3E)_3O]^+$ and $[(R_3E)_2OH]^+$ derivatives. Energy offsets between attractions and repulsions are also displayed.

Species	E	R	∑LP(O)→σ*(E-R) (kcal mol^{-1})	∑LP(O)→d(E) (kcal mol^{-1})	∑LP(O)→σ*(E-R) + LP(O)→d(E) (kcal mol^{-1})	∑ LP(O)···σ(E-R) (kcal mol^{-1})	ΔE (attraction-repulsion) (kcal mol^{-1})
$[(R_3E)_3O]^+$	C	H	5.66	–	**5.66**	**13.73**	**-8.1**
		Me	4.76	–	**4.76**	**12.09**	**-7.4**
	Si	H	4.74	2.05	**6.79**	**7.62**	**-0.8**
		Me	5.03	1.85	**6.88**	**6.97**	**-0.1**
	Ge	H	3.74	1.42	**5.16**	**6.04**	**-0.9**
		Me	4.05	0.85	**4.90**	**5.29**	**-0.4**
	Sn	H	2.72	0.77	**3.49**	**4.31**	**-0.8**
		Me	3.24	0.93	**4.17**	**4.85**	**-0.7**
$[(R_3E)_2OH]^+$	C	H	5.35	–	**5.35**	**12.70**	**-7.4**
		Me	5.11	–	**5.11**	**11.59**	**-6.5**
	Si	H	4.65	1.78	**6.43**	**7.05**	**-0.6**
		Me	5.01	1.62	**6.31**	**6.31**	**0.5**
	Ge	H	3.53	1.07	**4.60**	**4.46**	**0.1**
		Me	4.24	0.31	**4.55**	**4.74**	**-0.2**
	Sn	H	2.41	0.65	**2.41**	**3.65**	**-0.6**
		Me	2.81	0.71	**3.52**	**3.99**	**-0.5**

Hydrogenated and Methylated Ethers

Table S3. NBO DEL optimized values of the E-O-E angles and the E-O bond distances, obtained by removing the attractions generated by $LP_1(O)$, in model $(H_3E)_2O$ compounds – removal of hyperconjugative $\sum LP_1(O)\rightarrow\sigma^*(E\text{-}H)$ interactions, and of $\sum[LP_1(O)\rightarrow\sigma^*(E\text{-}H) + LP_1(O)\rightarrow d(E)]$ interactions are presented separately. The equilibrium E-O-E angles and E-O bond lengths, as well as the sum of covalent radii of E and O atoms (*Cordero et. al., Dalton Trans. 2008, 21, 2832*), are displayed for further comparisons.

$(H_3E)_2O$	*Equilibrium Geometries*		*NBO DEL optimizations $LP_1(O)\rightarrow\sigma^*(E\text{-}H)$ removed*		*NBO DEL optimizations $LP_1(O)\rightarrow\sigma^*(E\text{-}H) + LP_1(O)\rightarrow d(E)$ removed*		*Ref. Val.*
E	**E-O-E (°)**	**E-O (Å)**	**E-O-E (°)**	**E-O (Å)**	**E-O-E (°)**	**E-O (Å)**	**Σ*cov*(E+O) (Å)**
C	112.1	1.399	**107.5**	**1.439**	**-**	**-**	*1.42*
Si	148.7	1.634	**120.1**	**1.684**	**112.2**	**1.715**	*1.77*
Ge	128.1	1.773	**116.8**	**1.808**	**114.0**	**1.827**	*1.86*
Sn	133.5	1.954	**120.1**	**1.985**	**117.5**	**1.998**	*2.05*

Table S4. NBO DEL optimized values of the E-O-E angles and the E-O bond distances, obtained by removing the attractions generated by both lone pair electrons (*i.e.* $LP_1(O)$ + $LP_2(O)$ orbitals), in model $(H_3E)_2O$ compounds – deletion of $\sum[LP_1(O)\rightarrow\sigma^*(E\text{-}H) + LP_2(O)\rightarrow\sigma^*(E\text{-}H)]$ interactions, and of $\sum[LP_1(O)\rightarrow\sigma^*(E\text{-}H) + LP_1(O)\rightarrow d(E) + LP_2(O)\rightarrow\sigma^*(E\text{-}H) + LP_2(O)\rightarrow d(E)$ interactions are illustrated independently. The equilibrium E-O-E angles and E-O bond lengths, as well as the sum of covalent radii of E and O atoms (*Cordero et. al., Dalton Trans. 2008, 21, 2832*), are displayed as reference values.

$(H_3E)_2O$	*Equilibrium Geometries*		*NBO DEL optimizations* $LP_1(O)\rightarrow\sigma^*(E\text{-}H) + LP_2(O)\rightarrow\sigma^*(E\text{-}H)$ *removed*		*NBO DEL optimizations* $LP_1(O)\rightarrow\sigma^*(E\text{-}H) + LP_1(O)\rightarrow d(E) + LP_2(O)\rightarrow\sigma^*(E\text{-}H) + LP_2(O)\rightarrow d(E)$ *removed*		*Ref. Val.*
E	**E-O-E (°)**	**E-O (Å)**	**E-O-E (°)**	**E-O (Å)**	**E-O-E (°)**	**E-O (Å)**	**Σ*cov*(E+O) (Å)**
C	112.1	1.399	**107.5**	**1.509**	**-**	**-**	*1.42*
Si	148.7	1.634	**119.5**	**1.729**	**111.9**	**1.800**	*1.77*
Ge	128.1	1.773	**115.7**	**1.856**	**113.7**	**1.874**	*1.86*
Sn	133.5	1.954	**119.0**	**2.019**	**117.1**	**2.037**	*2.05*

Discussions on the impact of LP (O)→d(E) donations on the bonding mechanism of E-O-E linkages (E = Si, Ge, Sn)

NBO DEL optimizations performed on model $(H_3E)_2O$ inorganic derivatives, implying the removal of $LP_1(O)\rightarrow\sigma^*(E\text{-}H)$ and $LP_1(O)\rightarrow d(E)$ effects, modifies drastically the geometries of these species with respect to their initial structures (Tables S3). In terms of E-O-E angles, NBO DEL calculated values of 112.2° for $(H_3Si)_2O$, 114.0° for $(H_3Ge)_2O$ and 117.5° for $(H_3Sn)_2O$, are significantly narrower than analogue angles in the equilibrium structures. But if we are to remove the $LP_1(O)\rightarrow\sigma^*(E\text{-}H)$ hyperconjugations only, without the $LP_1(O)\rightarrow d(E)$ effects, it results into E-O-E angles considerably wider than in the previous case: 120.1° for $(H_3Si)_2O$, 116.8° for $(H_3Ge)_2O$ and 120.1° for $(H_3Sn)_2O$.

On the other hand, $LP_1(O)\rightarrow d(E)$ and $LP_2(O)\rightarrow d(E)$ donations are as well responsible, although to a lesser extent than the hyperconjugations, for the short E-O bond distances of inorganic ethers. In this regard, it is highlight in Table S4 that E-O bond lengths computed by means of NBO DEL techniques display considerably different lengths if such p→d back-bonding interactions are deleted or not.

In summary, the present NBO DEL results reinforce the idea that p→d interactions display non-negligible contributions into the bonding mechanism of inorganic ethers.

Fluorinated and Chlorinated Ethers

Table S5. Equilibrium E-O-E angles and E-O bond distances in model H_3E-O-EH_2X systems (X = F, Cl). Calculated offsets between attractions and repulsions (*i.e.* ATR-REP) are presented (such computed values are reported per E-O bond and per E-O-E unit respectively). Values obtained by summing the covalent radii of E and O atoms are set as reference for the equilibrium E-O bond distances (for covalent radii see *Cordero et. al., Dalton Trans. 2008, 21, 2832*).

Species	E	R	E-O-E (°)	(H_3)E-O (Å)	(XH_2)E-O (Å)	Σ*cov*(E+O) (Å)	(ATR-REP) / (H_3)E-O bond (kcal/mol)	(ATR-REP) / (XH_2)E-O bond (kcal/mol)	(ATR-REP) / E-O-E unit (kcal/mol)
H_3E-O-EH_2F	**C**	H	114.0	1.414	1.363	*1.42*	**-8.4**	**8.0**	**-0.4**
	Si	H	149.9	1.640	1.616	*1.77*	**13.2**	**17.2**	**30.4**
	Ge	H	128.8	1.784	1.748	*1.86*	**2.4**	**6.3**	**8.7**
	Sn	H	130.1	1.970	1.929	2.05	**0.6**	**6.5**	**7.1**
H_3E-O-EH_2Cl	**C**	H	114.5	1.412	1.361	*1.42*	**-9.0**	**6.9**	**-2.1**
	Si	H	148.4	1.642	1.619	*1.77*	**10.1**	**14.5**	**24.6**
	Ge	H	128.7	1.785	1.752	*1.86*	**3.7**	**7.7**	**11.4**
	Sn	H	132.3	1.969	1.932	2.05	**2.5**	**4.5**	**7.0**

Table S6. Equilibrium E-O-E angles and E-O bond distances in model H_3E-O-EX_3 systems (X = F, Cl). Calculated offsets between attractions and repulsions (*i.e.* ATR-REP) are displayed (computed values are reported per E-O bond and per E-O-E unit). Values obtained by summing the covalent radii of E and O atoms are set as reference for the equilibrium E-O bond distances (for covalent radii see *Cordero et. al., Dalton Trans. 2008, 21, 2832*).

Species	E	R	E-O-E (°)	(H_3)E-O (Å)	(X_3)E-O (Å)	Σ*cov*(E+O) (Å)	(ATR-REP) / (H_3)E-O bond (kcal/mol)	(ATR-REP) / (X_3)E-O bond (kcal/mol)	(ATR-REP) / E-O-E unit (kcal/mol)
H_3E-O-EF_3	**C**	H	115.7	1.426	1.335	*1.42*	**-10.9**	**18.0**	**7.1**
	Si	H	158.8	1.645	1.585	*1.77*	**9.1**	**23.4**	**32.6**
	Ge	H	130.9	1.802	1.710	*1.86*	**2.4**	**14.8**	**17.2**
	Sn	H	133.1	1.990	1.893	2.05	**1.7**	**10.6**	**12.3**
H_3E-O-ECl_3	**C**	H	118.0	1.424	1.338	*1.42*	**-10.9**	**18.9**	**7.0**
	Si	H	151.2	1.649	1.598	*1.77*	**9.1**	**23.4**	**32.5**
	Ge	H	129.5	1.798	1.728	*1.86*	**2.4**	**14.8**	**17.2**
	Sn	H	132.8	1.984	1.906	2.05	**1.7**	**10.6**	**12.3**

Table S7. Calculated E-O-E angles and E-O bond lengths for $(X_3E)_2O$ (X = H, F, Cl) model species; NPA charges are computed for the E and O atoms of these model systems. The sum of covalent radii of E and O atoms (*Cordero et. al., Dalton Trans. 2008, 21, 2832*) are set as reference values for equilibrium E-O lengths.

Species	E	E-O-E (°)	E-O (Å)	Σ*cov*(E+O) (Å)	*q*(E)	*q*(O)
$(H_3E)_2O$	**C**	112.1	1.399	*1.42*	-0.272	-0.483
	Si	148.7	1.634	*1.77*	1.204	-1.236
	Ge	128.1	1.773	*1.86*	1.081	-1.198
	Sn	133.5	1.954	*2.05*	1.252	-1.276
$(F_3E)_2O$	**C**	120.2	1.371	*1.42*	1.138	-0.516
	Si	165.8	1.596	*1.77*	2.547	-1.317
	Ge	134.0	1.730	*1.86*	2.567	-1.295
	Sn	135.9	1.916	*2.05*	2.709	-1.364
$(Cl_3E)_2O$	**C**	127.2	1.383	*1.42*	0.129	-0.511
	Si	155.4	1.612	*1.77*	1.655	-1.270
	Ge	134.0	1.749	*1.86*	1.703	-1.255
	Sn	135.3	1.928	*2.05*	1.888	-1.288

Table S8. Equilibrium H-E-E-H torsion angles (*i.e.* H atoms = grey spheres in Figure 6 in the Main Text) within model $(H_3E)_2O$, $(XH_2E)_2O$ and $(X_2HE)_2O$ compounds (X = F or Cl).

Species	$(H_3E)_2O$	$(FH_2E)_2O$	$(F_2HE)_2O$	$(ClH_2E)_2O$	$(Cl_2HE)_2O$
E	**H-E-E-H (°)**	**H-E-E-H (°)**	**H-E-E-H (°)**	**H-E-E-H (°)**	**H-E-E-H (°)**
C	0.0	34.7	45.2	17.3	52.6
Si	0.2	30.1	71.6	29.0	50.4
Ge	0.1	43.3	64.1	34.9	55.6
Sn	0.2	61.3	68.5	52.5	60.1

Table S9. Calculated attraction-repulsion offsets in case of $LP_1(O)$, $LP_2(O)$ and $LP_1(O)+LP_2(O)$ are displayed for model $(H_3E)_2O$, $(XH_2E)_2O$ and $(X_2HE)_2O$ compounds (X = F or Cl)

Species	E	$LP_1(O)$ (attraction-repulsion) / E-O-E unit (kcal mol^{-1})	$LP_2(O)$ (attraction-repulsion) / E-O-E unit (kcal mol^{-1})	$LP_1(O) + LP_2(O)$ (attraction-repulsion) / E-O-E unit (kcal mol^{-1})
$(H_3)_{E2}O$	**C**	-7.1	-7.3	**-14.4**
	Si	8.7	13.5	**22.2**
	Ge	1.6	9.2	**10.7**
	Sn	1.0	5.9	**6.9**
$(ClH_2E)_2O$	**C**	-6.9	11.7	**4.8**
	Si	8.5	17.3	**25.8**
	Ge	2.4	10.9	**13.3**
	Sn	1.6	7.5	**9.1**
$(Cl_2HE)_2O$	**C**	-0.6	17.3	**16.7**
	Si	13.7	19.6	**33.3**
	Ge	4.8	14.0	**18.8**
	Sn	2.9	11.3	**14.2**

Acyclic Oligomers

Table S10. Attraction-repulsion energy differences per E-O bonds within model H_3E-O-EH_2-O-EH_3 oligomers - offsets are reported for both *internal* and *external* E-O bonds (for clarity see also Figure 8 in the Main Text); in addition, offset value are displayed for the particular cases of $LP_1(O)$, $LP_2(O)$, and $LP_1(O)+LP_2(O)$ respectively

Species	E	$LP_1(O)$ offset / int E-O bond (kcal mol^{-1})	$LP_2(O)$ offset / int E-O bond (kcal mol^{-1})	$LP_1(O)+LP_2(O)$ offset / int E-O bond (kcal mol^{-1})	$LP_1(O)$ offset / ext E-O bond (kcal mol^{-1})	$LP_2(O)$ offset / ext E-O bond (kcal mol^{-1})	$LP_1(O)+LP_2(O)$ offset / ext E-O bond (kcal mol^{-1})
H_3E-O-EH_2-O-EH_3	**C**	-3.7	5.1	**1.4**	-4.0	-10.8	**-14.8**
	Si	4.8	10.2	**15.0**	4.6	6.4	**11.0**
	Ge	0.8	7.2	**8.0**	0.7	3.4	**4.1**
	Sn	0.6	4.2	**4.8**	0.1	2.4	**2.5**

Table S11. Attraction-repulsion energy differences per E-O-E unit within model H_3E-O-EH_2-O-EH_2-O-EH_3 oligomers - offsets are reported for both the *internal* and *external* E-O-E angles of these acyclic oligomers (for clarity see also Figure 8 in the Main Text); in addition, offset value are displayed for the particular cases of $LP_1(O)$, $LP_2(O)$, and $LP_1(O)+LP_2(O)$ respectively

Species	E	$LP_1(O)$ offset / int E-O-E (kcal mol^{-1})	$LP_2(O)$ offset / int E-O-E (kcal mol^{-1})	$LP_1(O)+LP_2(O)$ offset / int E-O-E (kcal mol^{-1})	$LP_1(O)$ offset / ext E-O-E (kcal mol^{-1})	$LP_2(O)$ offset / ext E-O-E (kcal mol^{-1})	$LP_1(O)+LP_2(O)$ offset / ext E-O-E (kcal mol^{-1})
$(H_3E$-O-$EH_2)_2O$	**C**	-8.1	8.1	**0.0**	-8.0	1.2	**-6.8**
	Si	10.8	27.2	**38.1**	9.9	17.2	**27.1**
	Ge	2.0	17.5	**19.5**	1.9	10.5	**12.4**
	Sn	2.5	7.4	**9.9**	1.4	5.4	**6.8**