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

Supplementary Information

The preferred geometry of hydroperoxides is the result of an interplay between electrostatic and hyperconjugative effects

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Computational Details

All potential energy curves (PEC) were optimized at the M06-2X/aug-cc-pVTZ level using ORCA 4.0.1[1,2] by scanning the H-O-O-R dihedral angle from 0 to 180° in steps of 10°. For the peroxide $HOOC(CH_3)_3$, the fixed O1-O3-C4-C5 dihedral angle (Figure S1f) at 180° was also included throughout the scan.

The Natural Bond Orbitals analysis were carried out using Gaussian09 Rev D.01[3] and NBO6.0[4] at the M06-2X/aug-cc-pVTZ level by single point calculations over the geometries of the optimized potential energy curves. The curves of NBO Energetic Analysis were calculated by the deletion of all non-Lewis orbitals.

Individual natural coulombic interactions (Figure S3) for each point of the PEC were calculated from the interatomic distances (R_{AB}) and the total atomic charges (Q_A and Q_B) given by the Natural Coulomb Electrostatics (NCE) analysis using the Equation S1 and a Python code (page S25). The sum of all calculated interactions was compared with the NCE Potential Energy of each structure to verify the validity of the numerical values.

$$E_{AB} = \frac{Q_A Q_B}{R_{AB}} \qquad \text{(S1)}$$

The individual hyperconjugative interactions (Figure S4) were analyzed using the data from the NBO Energetic Analysis output (Second Order Perturbation Theory Analysis List) setting the threshold for printing equal to 0 kcal mol^{-1} and excluding all interactions involving Rydberg (RY) and Core (CR) orbitals. To decrease the number of interactions shown in the graphs and make the qualitative analysis easily, some interactions were added into a new curve called “Others”. All interactions with the amplitude (the difference between the maximum and the minimum values of energy) lower than a cutoff value were chosen to “Others” curve and, a Python code was used to calculate the number of the remaining interactions and the amplitude of the “Others” curve in the function of the cutoff value (Figure S8) to set the best cutoff value for each molecule.

The individual steric interactions (Tables S5 and S6) were analyzed using the data from the NBO Natural Steric Analysis output setting the threshold for printing equal to 0 kcal mol^{-1}.

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[1] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2012, **2**, 73–78.
[2] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2018, **8**, e1327.
[3] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
[4] F. Weinhold, C. R. Landis and E. D. Glendening, *Int. Rev. Phys. Chem.*, 2016, **35**, 399–440.

Table S1. Basis set mean absolute error (MAE) (in kcal mol^{-1}) obtained from single point calculations for the M06-2X functional on MP2/cc-pVTZ calculated geometries and using the DLPNO-CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ level as reference for compounds **1**-**7**.

Basis Set	HOOH	HOOF	HOOCl	HOOBr	$HOOCH_3$	$HOOC(CH_3)_3$	$HOOCF_3$	Average
cc-pVDZ	0.303	0.407	0.527	0.767	0.112	0.115	0.113	0.335
cc-pVTZ	0.062	0.361	0.132	0.318	0.123	0.166	0.130	0.185
cc-pVQZ	0.027	0.327	0.080	0.255	0.193	0.226	0.151	0.180
cc-pV5Z	0.035	0.296	0.045	0.224	0.172	0.207	0.144	0.160
aug-cc-pVDZ	0.097	0.079	0.480	0.658	0.122	0.163	0.119	0.245
aug-cc-pVTZ	0.027	0.266	0.073	0.215	0.153	0.175	0.148	0.151

Table S2. Methods mean absolute error (MAE) (in kcal mol^{-1}) obtained with the aug-cc-pVTZ basis set on MP2/cc-pVTZ calculated geometries and using the DLPNO-CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ level as reference for compounds **1**-**7**.

Method	HOOH	HOOF	HOOCl	HOOBr	$HOOCH_3$	$HOOC(CH_3)_3$	$HOOCF_3$	Average
B3LYP	0.067	0.567	0.395	0.552	0.037	0.055	0.126	0.257
B3LYP-D3(BJ)	0.067	0.568	0.396	0.553	0.046	0.092	0.127	0.264
HF	0.107	1.035	0.151	0.263	0.232	0.310	0.309	0.344
M06	0.073	0.655	0.497	0.481	0.177	0.216	0.126	0.318
M062X	0.027	0.266	0.073	0.215	0.153	0.175	0.148	0.151
MP2	0.065	0.118	0.129	0.151	0.074	0.081	0.059	0.097
PBE0	0.040	0.672	0.476	0.633	0.154	0.189	0.110	0.325

Table S3. Mean absolute error (MAE) obtained for the potential energy curves optimized at the M06-2X/aug-cc-pVTZ level and using the DLPNO-CCSD(T)/aug-cc-pVTZ level single point calculations as reference for compounds **1**-**7**.

Peroxide	**MAE (kcal mol^{-1})**
HOOH **(1)**	0.0222
HOOF **(2)**	0.2188
HOOCl **(3)**	0.0501
HOOBr **(4)**	0.1169
$HOOCH_3$ **(5)**	0.1175
$HOOC(CH_3)_3$ **(6)**	0.1175
$HOOCF_3$ **(7)**	0.1398

Table S4. Global minimum dihedral angle (in degrees) obtained from a potential energy curve built from a 0-180^{o} scan in steps of 10^{o} of the H-O-O-R dihedral angle for peroxides **1**-**7**. The *cis* (H-O-O-R dihedral angle of 0^{o}) and *trans* (H-O-O-R dihedral angle of 180^{o}) barrier relative energies (ΔE) in comparison to the obtained minimum geometry were calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level and are given in kcal mol^{-1}.

Peroxide/Disulfide	Min. dihedral (degrees)	ΔE_{cis}	ΔE_{trans}
HOOH **(1)**	110	7.22	1.21
HOOF **(2)**	80	8.00	8.69
HOOCl **(3)**	90	5.48	3.94
HOOBr **(4)**	90	5.60	3.34
$HOOCH_3$ **(5)**	120	5.59	0.29
$HOOC(CH_3)_3$ **(6)**	120	7.03	0.70
$HOOCF_3$ **(7)**	100	5.85	1.97

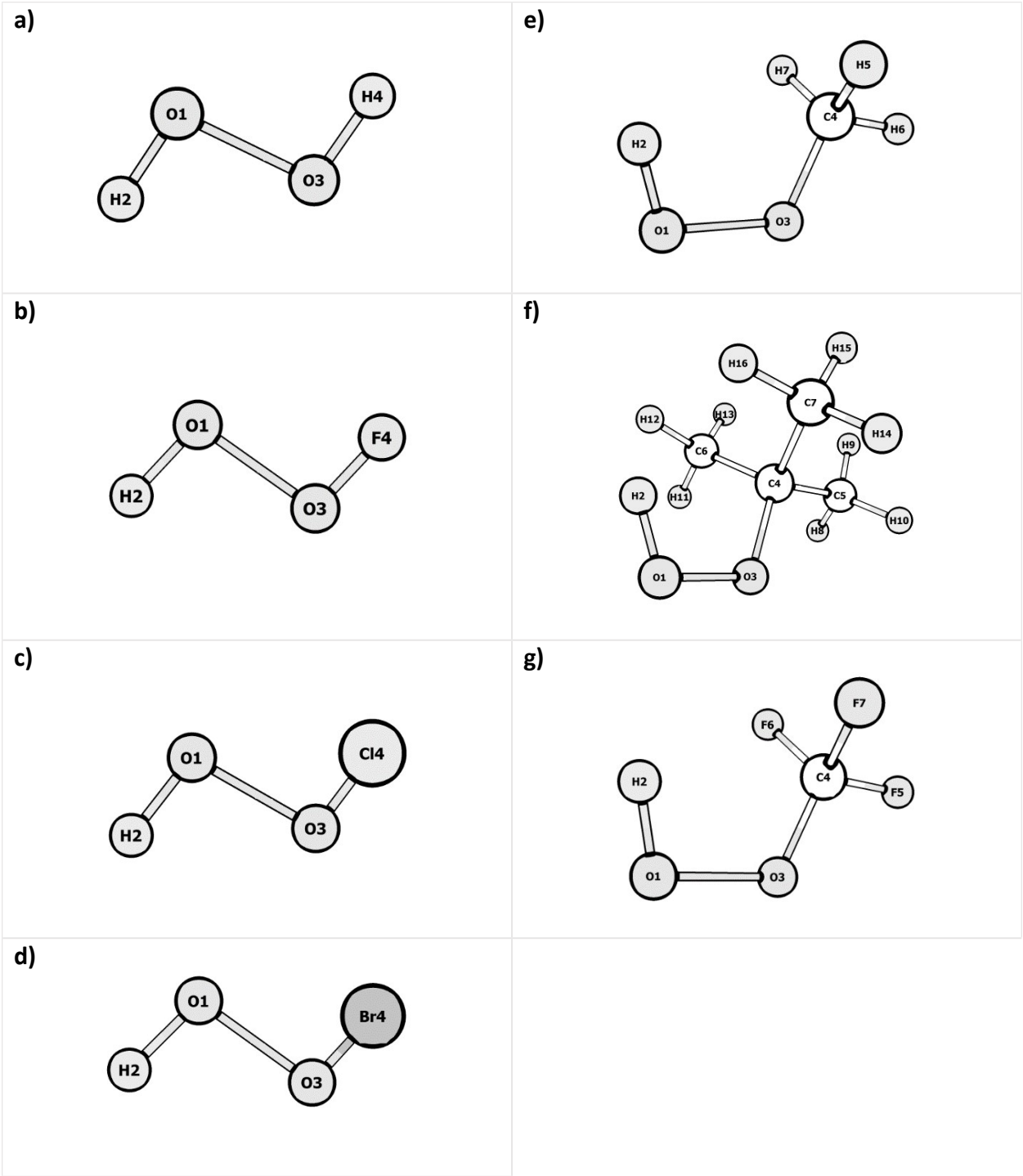


Figure S1. Atom numbering used for **a)** HOOH, **b)** HOOF **c)** HOOCl **d)** HOOBr **e)** HOOCH3 **f)** $HOOC(CH_3)_3$ and **g)** $HOOCF_3$ molecules.

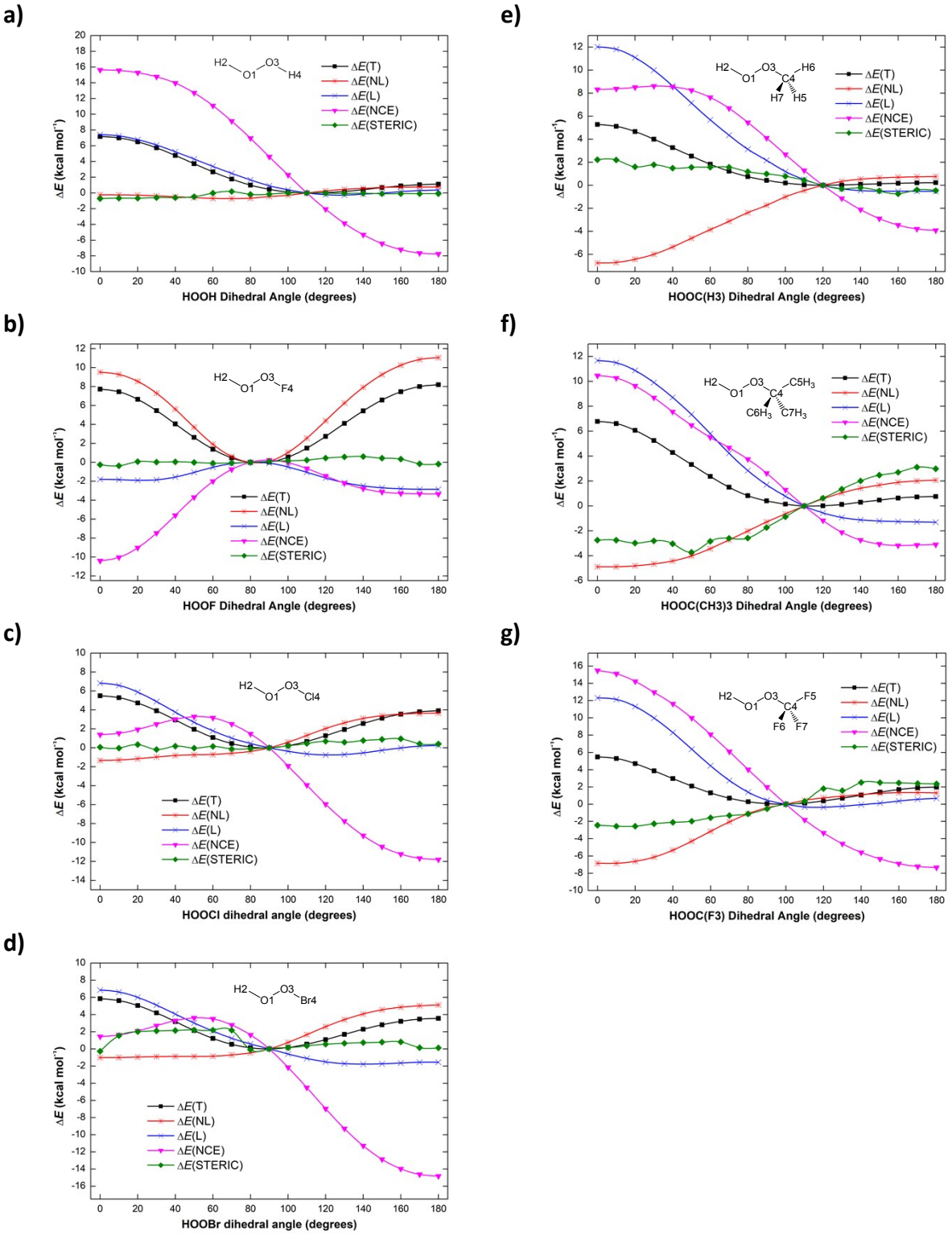


Figure S2. Total ΔE(T), non-Lewis ΔE(NL), Lewis ΔE(L), Natural Coulomb Electrostatic ΔE(NCE) and Natural steric analysis ΔE(STERIC) potential energy curves (kcal mol^{-1}) for **a)** HOOH, **b)** HOOF, **c)** HOOCl, **d)** HOOBr, **e)** HOOCH3, **f)** HOOC$(CH_3)_3$ and **g)** HOOCF_3 obtained at the M06-2X/aug-cc-pVTZ level from the NBO analysis.

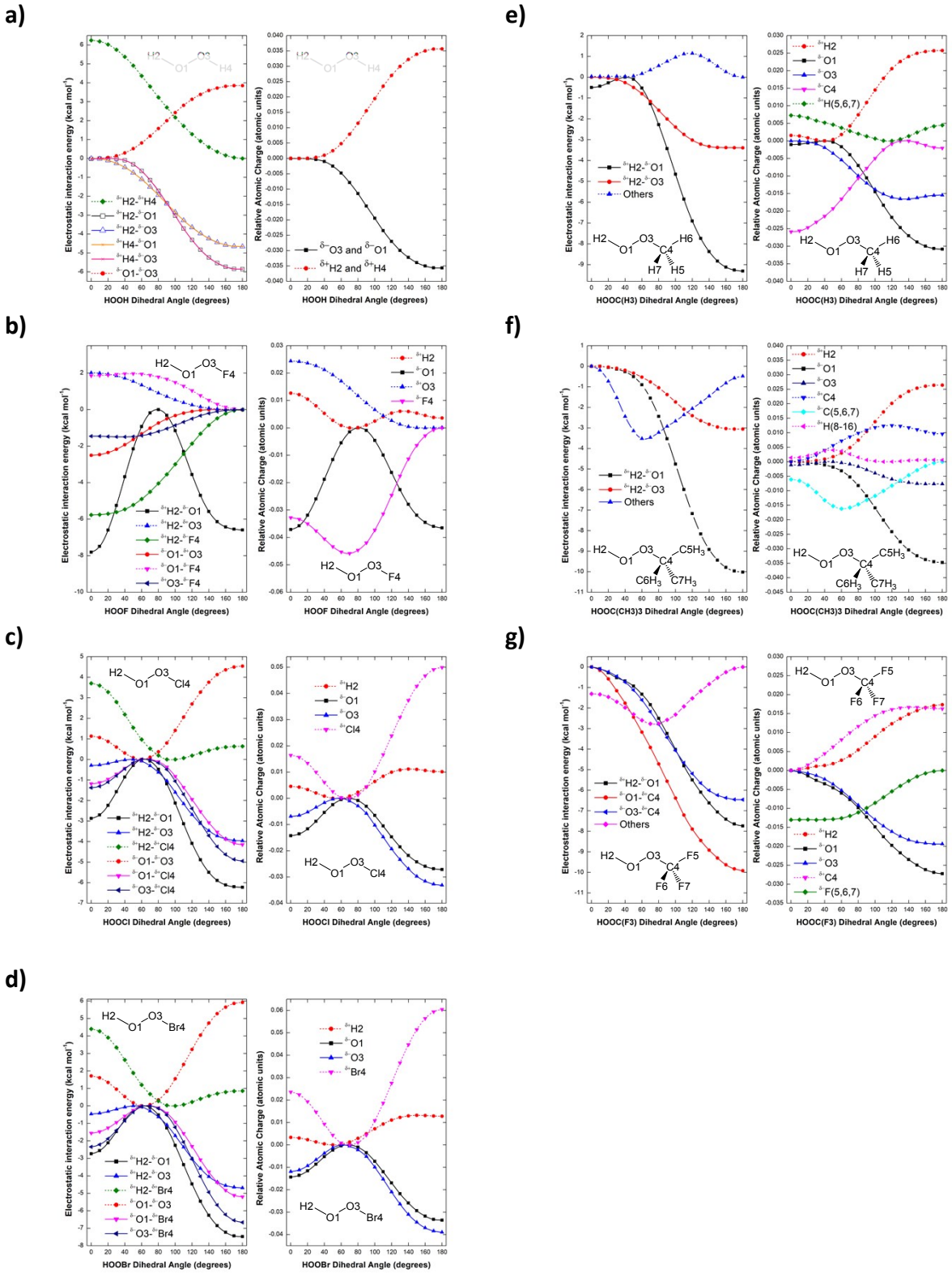


Figure S3. Individual natural coulombic potential energy curves (kcal mol^{-1}, left) and atomic charges (atomic units, right) for **a)** HOOH, **b)** HOOF, **c)** HOOCl, **d)** HOOBr, **e)** HOOCH3, **f)** $HOOC(CH_3)_3$ and **g)** $HOOCF_3$ obtained at the M06-2X/aug-cc-pVTZ level from the NBO analysis.

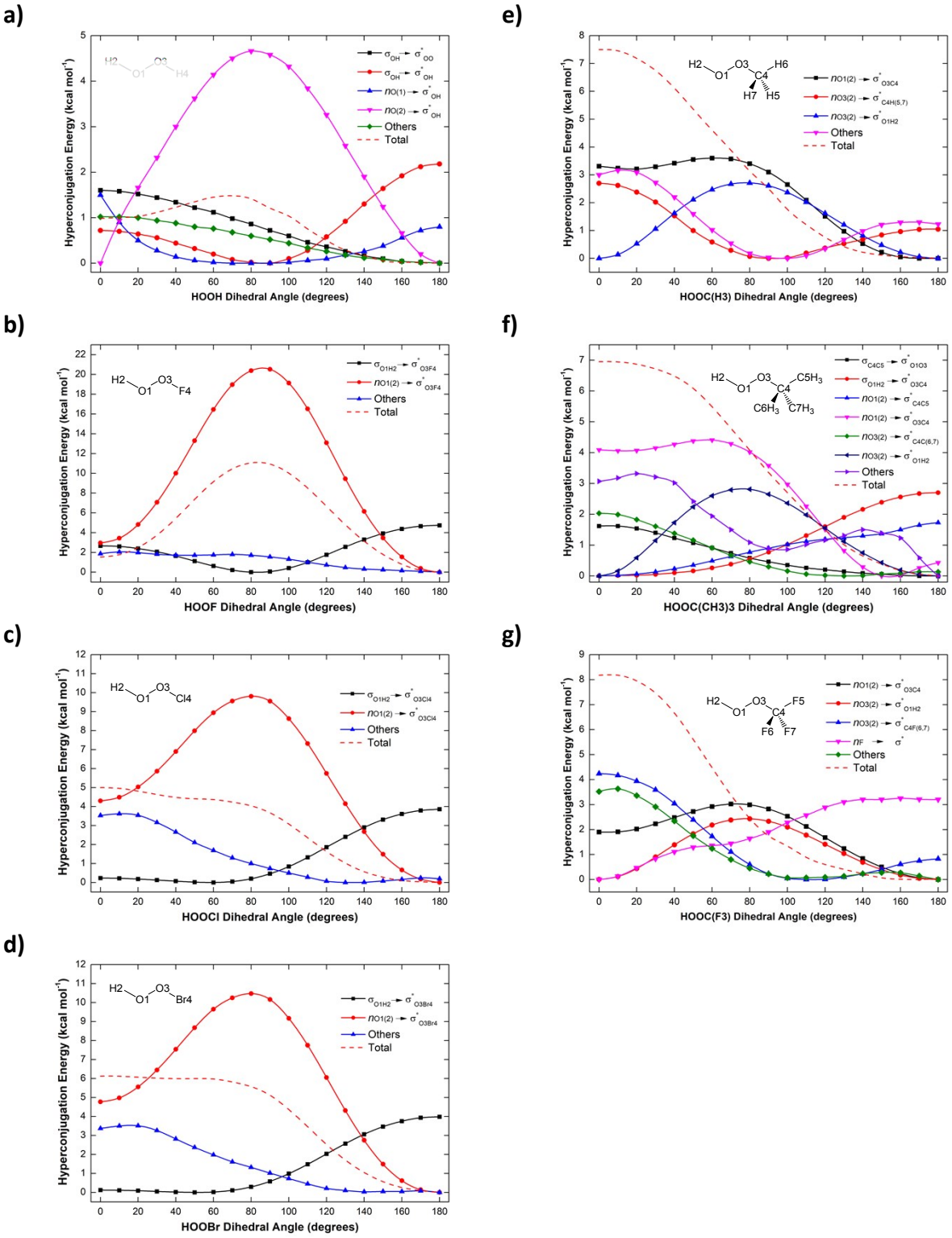


Figure S4. Hyperconjugation interaction energies (kcal mol^{-1}) for **a)** HOOH, **b)** HOOF, **c)** HOOCl, **d)** HOOBr, **e)** $HOOCH_3$, **f)** $HOOC(CH_3)_3$ and **g)** $HOOCF_3$ obtained at the M06-2X/aug-cc-pVTZ level from the NBO analysis.

Table S5. Steric interactions energies for $HOOC(CH_3)_3$ at *cis* and *trans* geometries obtained at the M06-2X/aug-cc-pVTZ level from the NBO analysis.

Interactions	E_{cis} (kcal mol^{-1})	E_{trans} (kcal mol^{-1})	ΔE (kcal mol^{-1})
n_{O1} - (σ_{OC}, σ_{CC}, σ_{CH})	1.82	16.39	14.57
σ_{O1H2} - (σ_{OC}, σ_{CC}, σ_{CH})	10.53	3.09	-7.44
Others	140.74	139.44	-1.31
Total	153.10	158.92	5.82

Table S6. Steric interactions energies for $HOOCF_3$ at *cis* and *trans* geometries obtained at the M06-2X/aug-cc-pVTZ level from the NBO analysis.

Interactions	E_{cis} (kcal mol^{-1})	E_{trans} (kcal mol^{-1})	ΔE (kcal mol^{-1})
n_{O1} - (σ_{CO}, σ_{CF}, n_F)	2.68	9.70	7.02
σ_{O1H2} - (σ_{CO}, σ_{CF}, n_F)	9.06	5.01	-4.05
Others	136.90	138.72	1.82
Total	148.64	153.43	4.79

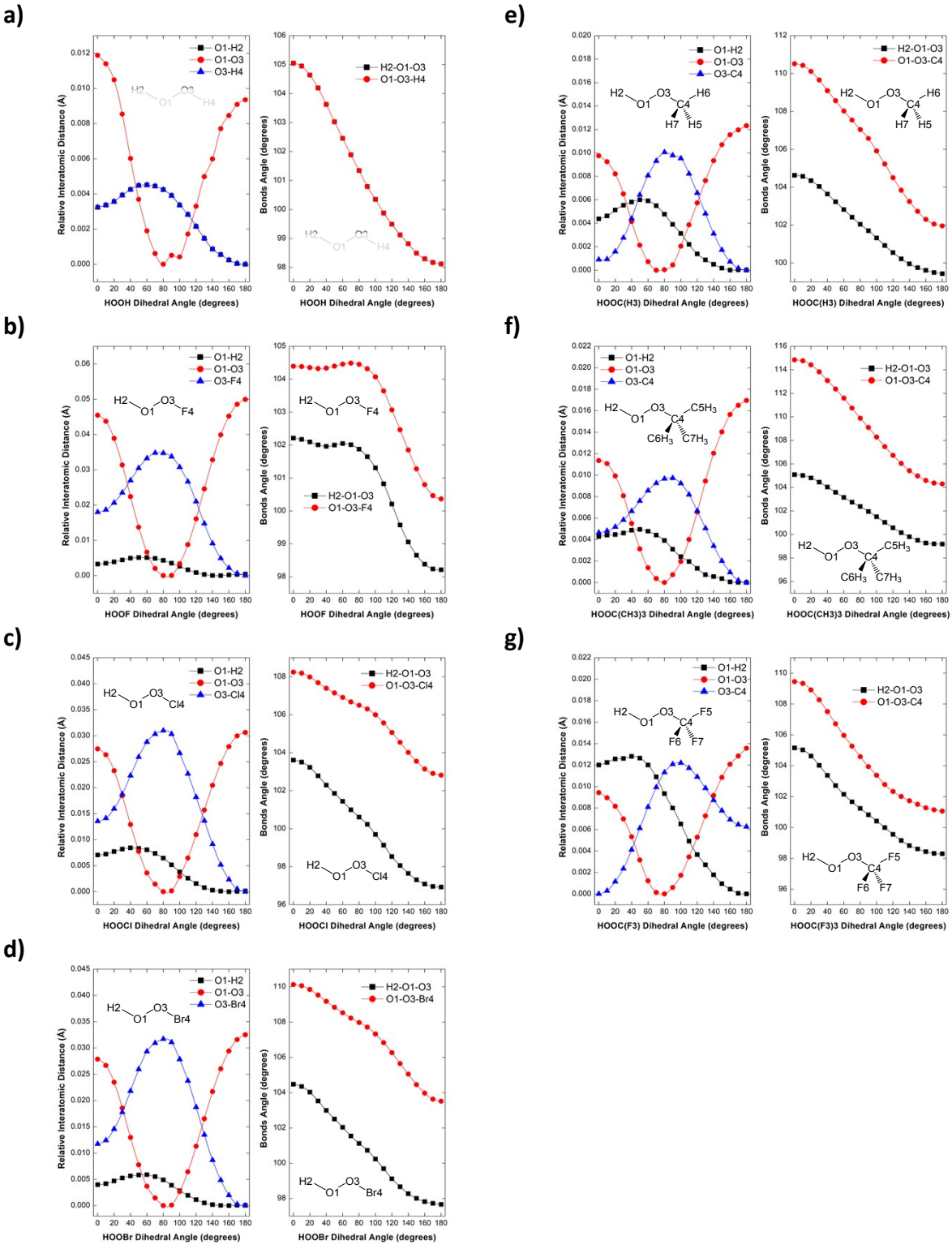
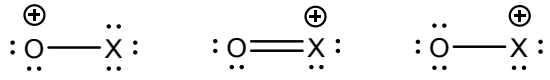


Figure S5. Relative Interatomic Distances and Bonds Angles for **a)** HOOH, **b)** HOOF, **c)** HOOCl, **d)** HOOBr, **e)** $HOOCH_3$, **f)** $HOOC(CH_3)_3$ and **g)** $HOOCF_3$ obtained at the M06-2X/aug-cc-pVTZ level.

For the stability analysis of the peroxides, the molecules and the respective radical fragments were optimized at the M06-2X/aug-cc-pVTZ and UM06-2X/aug-cc-pVTZ levels without any constraints using the software Gaussian 09. Frequencies calculations were carried out to evaluate the Gibbs and Enthalpy energies. The Natural Bond Orbitals calculations were carried out using the NBO6.0 program and the NBO open-shell analysis.[5] All the Lewis structures of the α and β spin sets are represented as analogues closed-shell structures.[6]

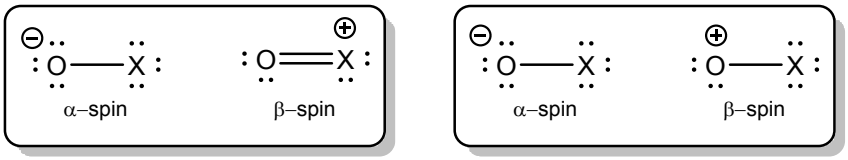
First, we carried out a Natural Resonance Theory (NRT)[7] analysis to evaluate the resonance structures of the radical fragments and their respective weights. For the FO•, ClO• and BrO• radicals we specified the following resonance structures for the β-spin set using the $NTRSTRB option:



STR1 STR2 STR3

The NRT results are shown in the Schemes S2 and S3 and, for the FO•, ClO• and BrO• radicals, the STR2 structure (with an O-X double bond) is the main resonance structure and with weights greater than 99.6%. That is a result of a radical stabilization via highly favourable hyperconjugative interactions between the lone pairs of the halogens atoms and the partially occupied O *p* orbital.

Finally, to allow the analysis and comparison of the (σ, *n*) → n_O hyperconjugative interactions in all radical fragments studied in this work, we specified the following structures for the radicals FO•, ClO• and BrO• using the $CHOOSE option and we carried out a DEL analysis.



Default NBO Search Specified with $CHOOSE

[5] J. E. Carpenter and F. Weinhold, *J. Mol. Struct. THEOCHEM*, 1988, **169**, 41–62.

[6] F. Weinhold, C. R. Landis and E. D. Glendening, *Int. Rev. Phys. Chem.*, 2016, **35**, 399–440.

[7] a) E. D. Glendening and F. Weinhold, *J. Comput. Chem.*, 1998, **19**, 593–609 b) E. D. Glendening and F. Weinhold, *J. Comput. Chem.*, 1998, **19**, 610–627. c) E. D. Glendening, J. K. Badenhoop and F. Weinhold, *J. Comput. Chem.*, 1998, **19**, 628–646.

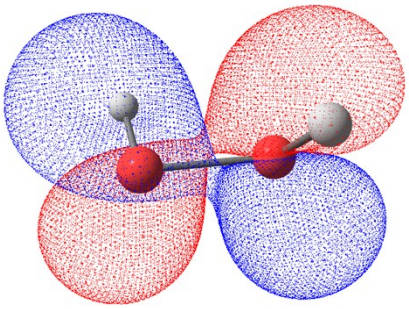
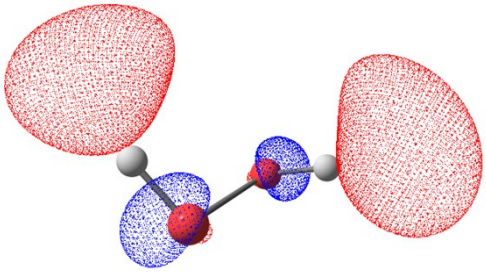
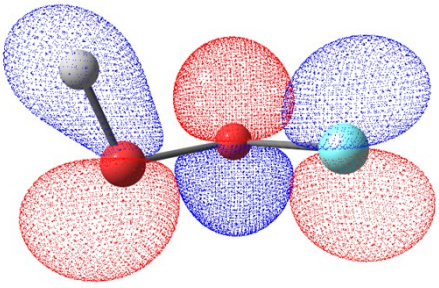
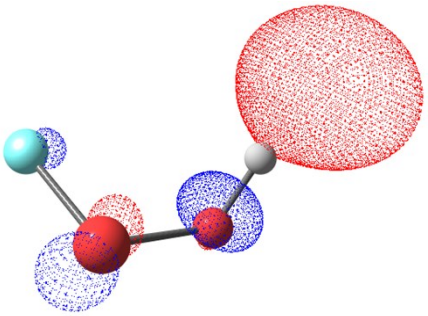
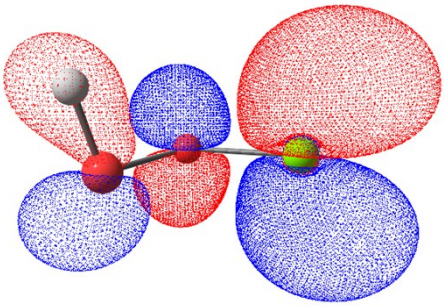
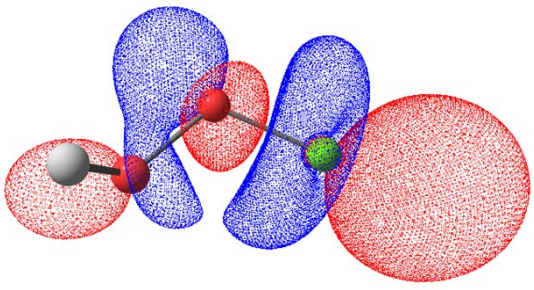
Table S7. Bond lengths, bonds angles and dihedral angle for molecules 1-7 obtained from the minimization at the M06-2X/aug-cc-pVTZ level using the software Gaussian 09.

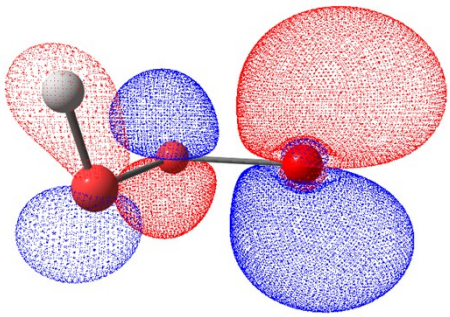
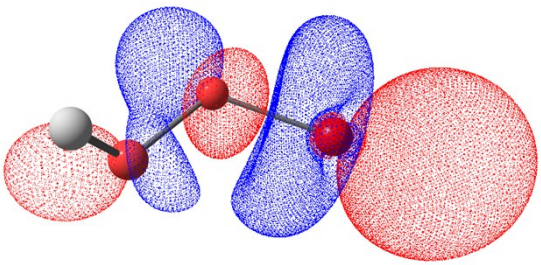
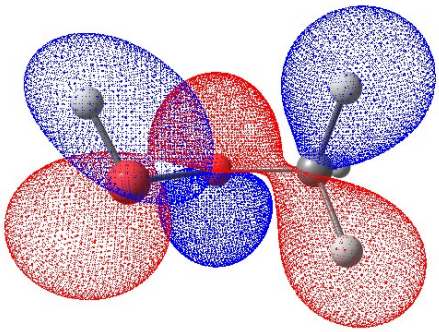
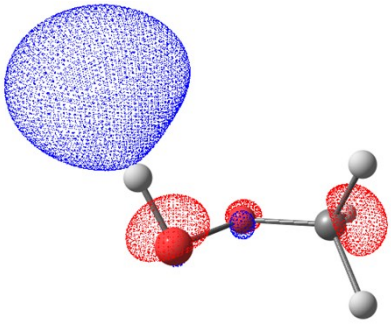
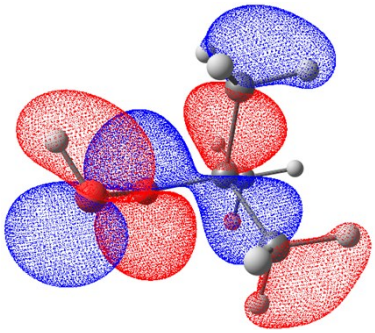
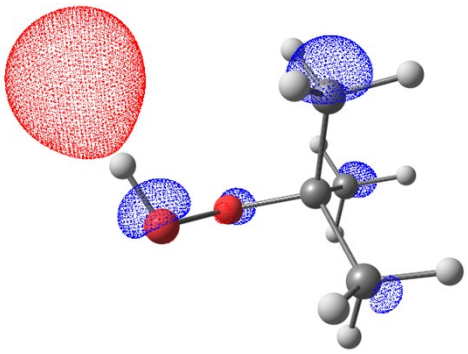
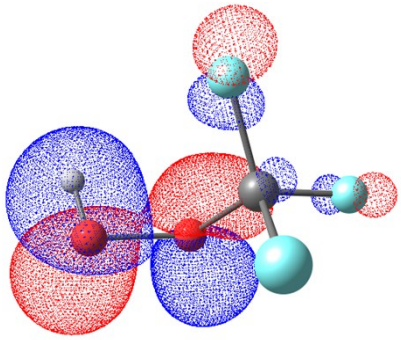
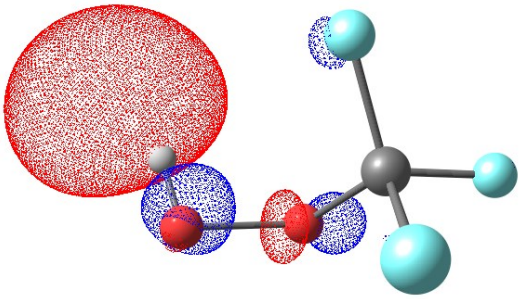
Molecule	Bond Length (Å)			Bonds Angle (degrees)		Dihedral Angle (degrees)
	O-O	H-O	O-R	H-O-O	O-O-R	HOOR
HOOH **(1)**	1.423	0.964	0.964	101.479	101.479	112.780
HOOF **(2)**	1.361	0.970	1.415	103.589	105.392	84.654
HOOCl **(3)**	1.399	0.968	1.693	102.626	109.309	88.211
HOOBr **(4)**	1.400	0.968	1.837	102.629	110.110	90.433
$HOOCH_3$ **(5)**	1.423	0.965	1.410	101.567	106.564	112.919
$HOOC(CH_3)_3$ **(6)**	1.422	0.964	1.438	101.545	109.286	108.829
$HOOCF_3$ **(7)**	1.414	0.967	1.368	101.785	107.257	98.353

Table S8. HOMO and LUMO energies for molecules **1**-**7** obtained from the minimization at the M06-2X/aug-cc-pVTZ level.

Molecule	HOMO (Eh)	LUMO (Eh)	HOMO-LUMO Gap (eV)
HOOH **(1)**	-0.3742	-0.0090	9.94
HOOF **(2)**	-0.4112	-0.0128	10.84
HOOCl **(3)**	-0.3656	-0.0413	8.83
HOOBr **(4)**	-0.3483	-0.0636	7.75
$HOOCH_3$ **(5)**	-0.3502	-0.0069	9.34
$HOOC(CH_3)_3$ **(6)**	-0.3424	-0.0080	9.10
$HOOCF_3$ **(7)**	-0.4319	-0.0144	11.36

Table S9. HOMO and LUMO surfaces[a] for molecules **1**-**7** obtained from the minimization at the M06-2X/aug-cc-pVTZ level.

Molecule	HOMO	LUMO
HOOH		
HOOF		
HOOCl		

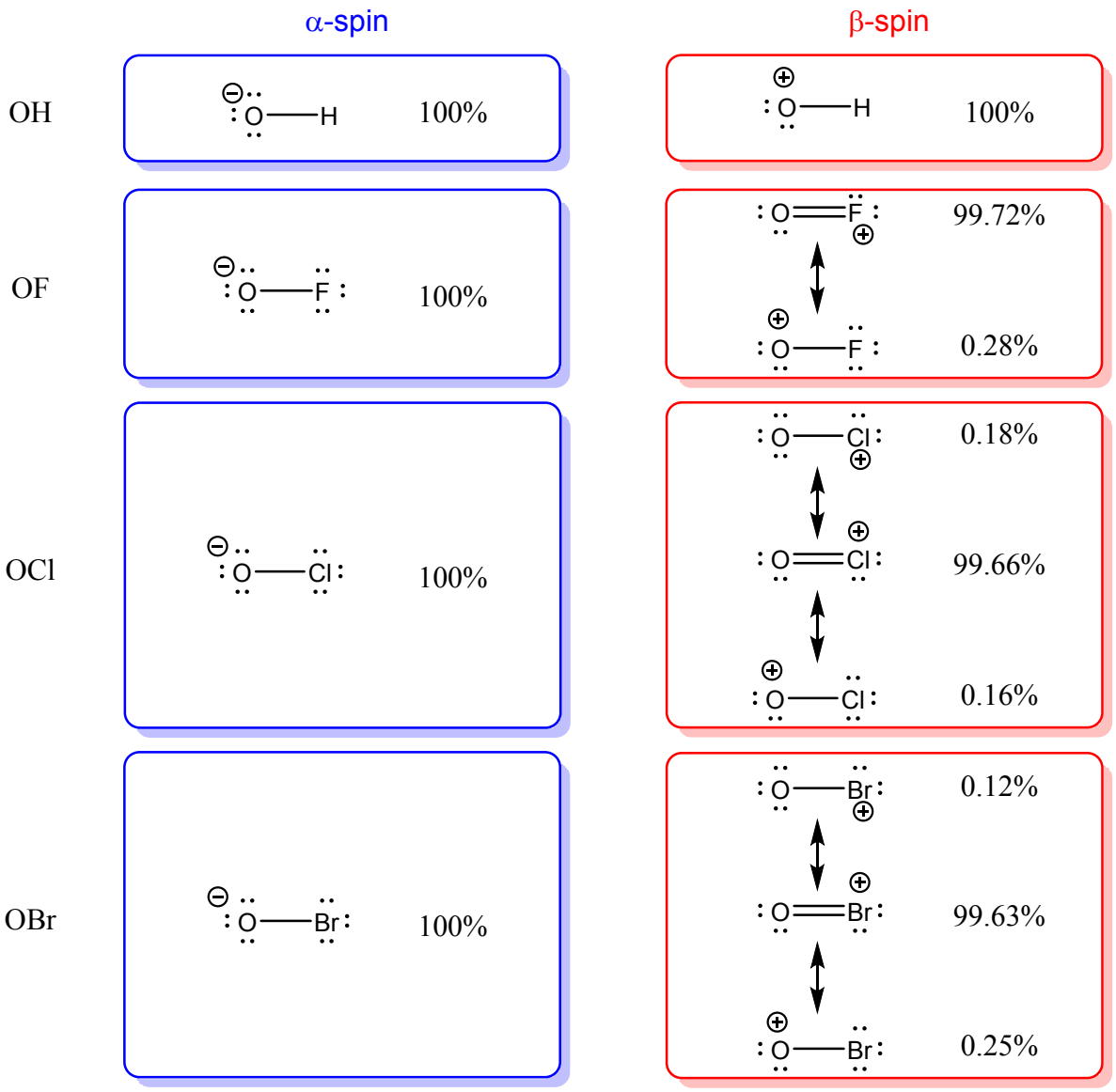
HOOBr		
$HOOCH_3$		
$HOOC(CH_3)_3$		
$HOOCF_3$		

[a] The molecular orbitals surfaces were rendered using the software Chemcraft 1.8 (Build 572b)[8] with a cube density of 20 map points per angstrom and the following contour values: 0.03 ($HOOC(CH_3)_3$), 0.036 (HOOH, HOOCl, HOOBr and $HOOCH_3$), 0.0432 ($HOOCF_3$) and 0.051840 (HOOF).

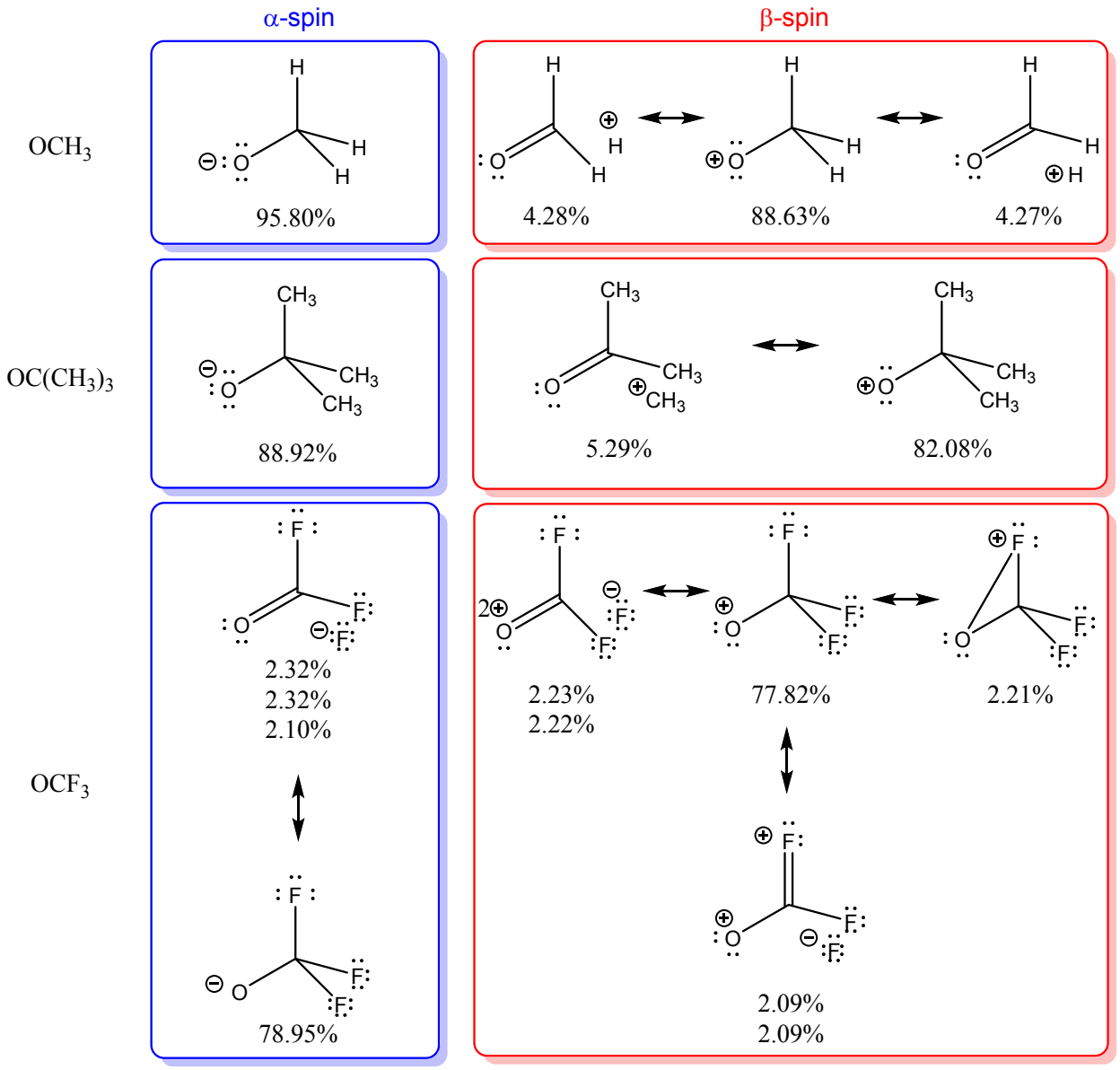
[8] G. A. Zhurko, Chemcraft - graphical program for visualization of quantum chemistry computations. Ivanovo, Russia, 2005. https://chemcraftprog.com

HOOH	⟶	HO·	+	·OH	$\Delta G^{\circ} = 40.01$	$\Delta H^{\circ} = 49.23$
HOOF	⟶	HO·	+	·OF	$\Delta G^{\circ} = 35.78$	$\Delta H^{\circ} = 45.42$
HOOCl	⟶	HO·	+	·OCl	$\Delta G^{\circ} = 24.98$	$\Delta H^{\circ} = 34.46$
HOOBr	⟶	HO·	+	·OBr	$\Delta G^{\circ} = 26.42$	$\Delta H^{\circ} = 35.88$
$HOOCH_3$	⟶	HO·	+	$\cdot OCH_3$	$\Delta G^{\circ} = 32.06$	$\Delta H^{\circ} = 42.64$
$HOOC(CH_3)_3$	⟶	HO·	+	$\cdot OC(CH_3)_3$	$\Delta G^{\circ} = 33.66$	$\Delta H^{\circ} = 44.44$
$HOOCF_3$	⟶	HO·	+	$\cdot OCF_3$	$\Delta G^{\circ} = 39.37$	$\Delta H^{\circ} = 50.72$

Scheme S1. Free Energy and Enthalpy variation of the O-O bond homolytic clivage for molecules 1-7 at the M06-2X/aug-cc-pVTZ level using the software Gaussian 09.



Scheme S2. Resonance structures and their weights obtained from the NTR analysis for HO•, FO•, ClO• and BrO• radical fragments. The structures of the spin sets are represented as analogues closed-shell structures.



Scheme S3. Main resonance structures (>2%) and their weights obtained from the NTR analysis for $H_3CO•$, $(CH_3)_3CO•$ and $F_3CO•$ radicals. The structures of the spin sets are represented as analogues closed-shell structures.

Table S10. Hyperconjugative interactions energies between bonds (σ) and lone pairs (n) and the O partially empty p orbital (n_O) of the β-spin set for HO•, FO•, ClO•, BrO•, H_3CO•, $(CH_3)_3CO$• and F_3CO• radicals obtained from the minimization at the M06-2X/aug-cc-pVTZ level using the software Gaussian 09.

Radical	Hyperconjugative Interactions (kcal mol^{-1})		
	$\sigma \rightarrow n_O$	$n \rightarrow n_O$	Total
OH	0.00	0.00	0.00
OF	0.00	48.23	48.23
OCl	0.00	119.09	119.09
OBr	0.00	104.93	104.93
OCH_3	20.73	0.00	20.73
$OC(CH_3)_3$	18.34	0.00	18.34
OCF_3	2.80	3.84	6.64

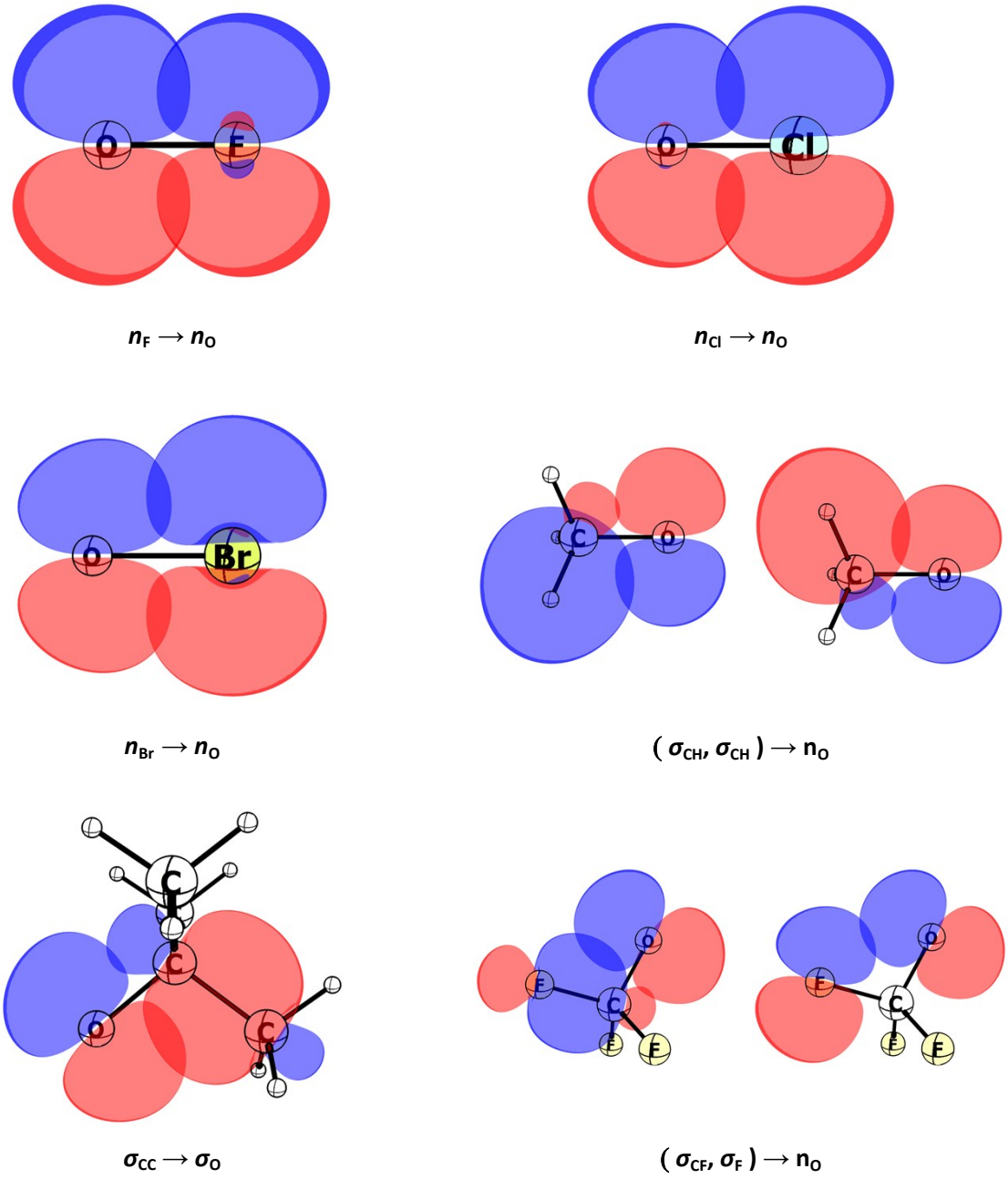


Figure S6. NBO surfaces of the main hyperconjugative interactions between bonds (σ) and lone pairs (n) and the O partially empty p orbital (n_O) of the β-spin set for FO•, ClO•, BrO•, H_3CO•, $(CH_3)_3CO$• and F_3CO• radicals obtained from the minimization at the M06-2X/aug-cc-pVTZ level using the software Gaussian 09. The molecular orbitals surfaces were rendered using the software Chemcraft 1.8 (Build 572b) with a cube density of 40 map points per angstrom and the following contour values: 0.06 (FO•, ClO•, BrO• and H_3CO•,) and 0.05 ($(CH_3)_3CO$• and F_3CO•).

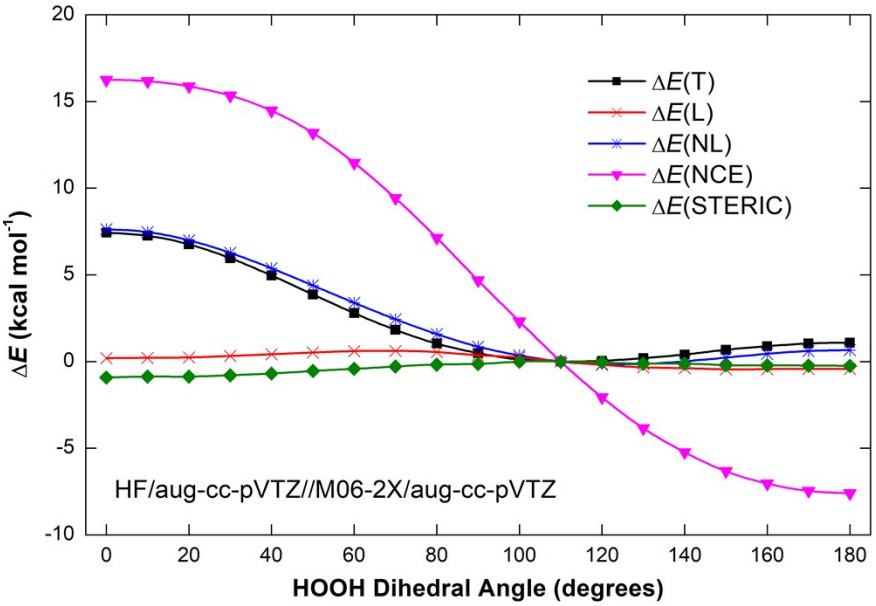


Figure S7. Total ΔE(T), non-Lewis ΔE(NL), Lewis ΔE(L), Natural Coulomb Electrostatic ΔE(NCE) and Natural steric analysis ΔE(STERIC) potential energy curves (kcal mol^{-1}) for HOOH obtained at the HF/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level from the NBO analysis

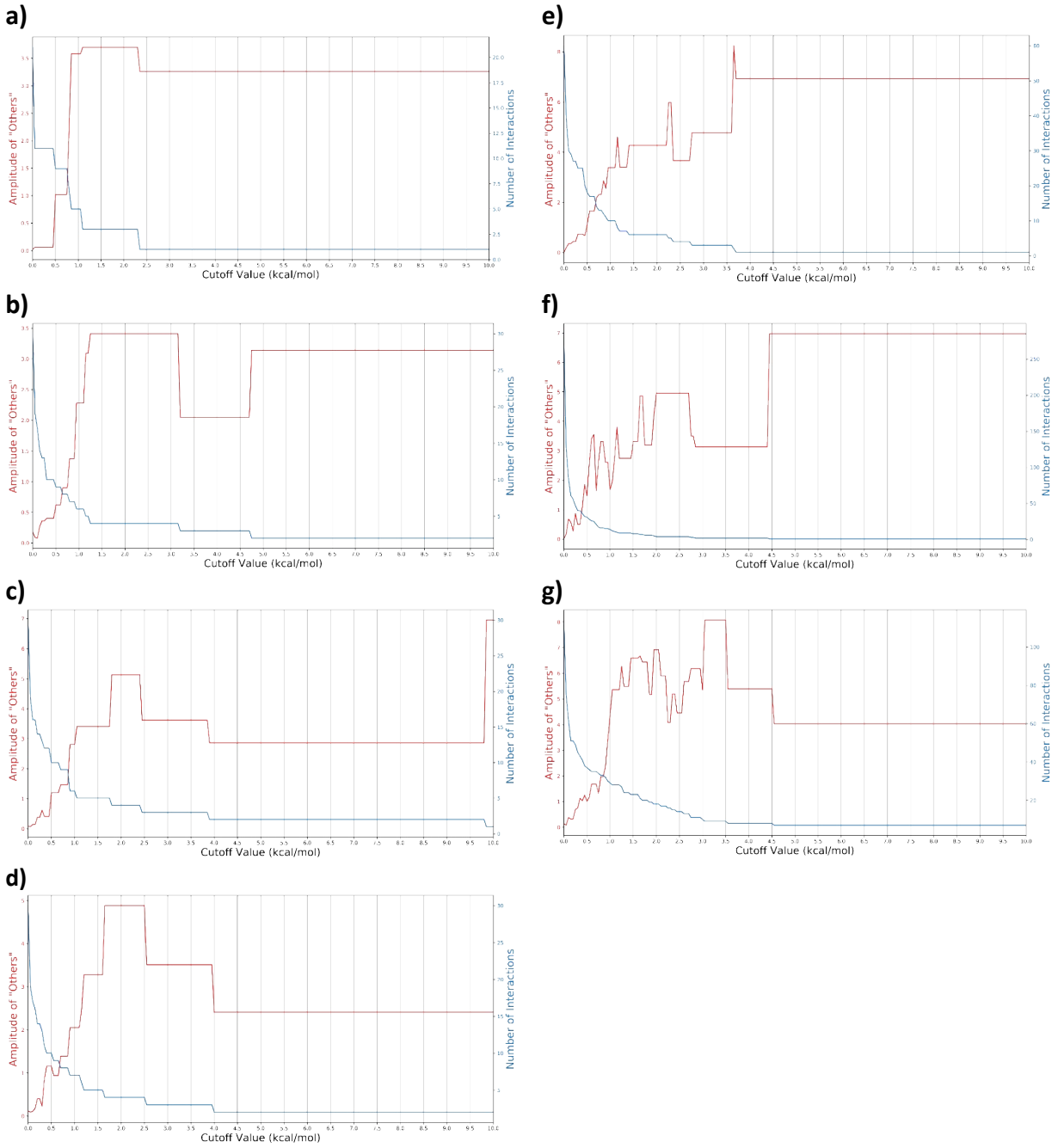


Figure S8. Number of remaining hyperconjugative interactions and the amplitude of the "Others" curve in the function of the cutoff value for **a)** HOOH, **b)** HOOF, **c)** HOOCl, **d)** HOOBr, **e)** HOOCH3, **f)** $HOOC(CH_3)_3$ and **g)** $HOOCF_3$ molecules.

```
import pandas as pd
import numpy as np
from itertools import combinations

input_data = pd.read_csv('HOOH_input.csv')

molecule_name = 'HOOH'
atoms_list = [ 'O1', 'H2', 'O3', 'H4']

interactions_list = list(combinations(atoms_list, 2))

interactions = np.zeros((19,len(interactions_list)))
distances = np.zeros((19,len(interactions_list)))

for n in range(0,len(interactions_list)):

    for i in range(0,19):
        a1 = interactions_list[n][0]
        a2 = interactions_list[n][1]
        dihedral = i * 10

        q1 = float(input_data.loc[input_data.Atom == a1].loc[input_data.Dihedral == dihedral]['Total'])
        q2 = float(input_data.loc[input_data.Atom == a2].loc[input_data.Dihedral == dihedral]['Total'])
        x1 = float(input_data.loc[input_data.Atom == a1].loc[input_data.Dihedral == dihedral]['X'])
        y1 = float(input_data.loc[input_data.Atom == a1].loc[input_data.Dihedral == dihedral]['Y'])
        z1 = float(input_data.loc[input_data.Atom == a1].loc[input_data.Dihedral == dihedral]['Z'])
        x2 = float(input_data.loc[input_data.Atom == a2].loc[input_data.Dihedral == dihedral]['X'])
        y2 = float(input_data.loc[input_data.Atom == a2].loc[input_data.Dihedral == dihedral]['Y'])
        z2 = float(input_data.loc[input_data.Atom == a2].loc[input_data.Dihedral == dihedral]['Z'])

        d = (((x1 - x2) ** 2) + ((y1 - y2) ** 2) + ((z1 - z2) ** 2)) ** (0.5)
        #interactions[i][n] = ((q1 * q2) / d) * 0.529177                #in a.u.
        interactions[i][n] = ((q1 * q2) / d) * 0.529177 * 627.509474     #in kcal mol-1
        distances[i][n] = d

charges = np.zeros((19,len(atoms_list)))

for n in range(0,len(atoms_list)):
    a1 = atoms_list[n]

    for i in range(0,19):
        dihedral = i * 10
        q = float(input_data.loc[input_data.Atom == a1].loc[input_data.Dihedral == dihedral]['Total'])
        charges[i][n] = q

np.savetxt(str(molecule_name + '_NCE_charges.csv'), charges, delimiter=",")
np.savetxt(str(molecule_name + '_NCE_interactions.csv'), interactions, delimiter=",")
np.savetxt(str(molecule_name + '_NCE_distances.csv'), distances, delimiter=",")
np.savetxt(str(molecule_name + '_NCE_interactions_list.txt'), interactions_list, fmt='%s', delimiter='-')
```

In the input file (csv format), the atoms are added in the lines with their total charge, cartesian coordinates and the dihedral angle of the corresponding geometry. As an example, the seven first lines for the HOOH input file:

Atom	Total	X	Y	Z	Dihedral
O1	-0.44844	0.000000	-0.718817	-0.103953	0
H2	0.44844	0.000000	-0.970354	0.831627	0
O3	-0.44844	0.000000	0.718817	-0.103953	0
H4	0.44844	0.000000	0.970354	0.831627	0
O1	-0.44841	-0.718486	-0.103618	0.011213	10
H2	0.44841	-0.969663	0.828946	-0.066466	10

Cartesians coordinates for molecules 1-7 in their *cis*, *trans* and global minimum geometries. Total energies (in atomic units) were obtained at the M06-2X/aug-cc-pVTZ level.

Molecule	*cis*				Minimum				*trans*			
HOOH	Total Energy (M06-2X/aug-cc-pVTZ) =-151.541973614				Total Energy (M06-2X/aug-cc-pVTZ) =-151.553414001				Total Energy (M06-2X/aug-cc-pVTZ) =-151.551627385			
	O	0.000000000	-0.718817000	-0.103953000	O	-0.704974000	-0.111497000	-0.060801000	O	0.000000000	-0.717548000	0.000000000
	H	0.000000000	-0.970354000	0.831627000	H	-0.991085000	0.634471000	0.486414000	H	0.955890000	-0.853887000	0.000000000
	O	0.000000000	0.718817000	-0.103953000	O	0.704973000	0.111497000	-0.060802000	O	0.000000000	0.717548000	0.000000000
	H	0.000000000	0.970354000	0.831627000	H	0.991093000	-0.634470000	0.486414000	H	-0.955890000	0.853887000	0.000000000
HOOF	Total Energy (M06-2X/aug-cc-pVTZ) =-250.678124723				Total Energy (M06-2X/aug-cc-pVTZ) =-250.690386023				Total Energy (M06-2X/aug-cc-pVTZ) =-250.677373944			
	O	1.135576000	-0.188247000	0.000000000	O	-1.086507000	-0.223563000	-0.122953000	O	-1.024800000	-0.385689000	0.000000000
	H	0.753756000	-1.084980000	-0.000001000	H	-1.192471000	-0.599610000	0.771093000	H	-1.789931000	0.213446000	0.000000000
	O	-0.018439000	0.628092000	0.000000000	O	-0.004741000	0.597335000	0.043297000	O	0.000000000	0.594455000	0.000000000
	F	-1.076761000	-0.270421000	0.000000000	F	1.102495000	-0.265618000	-0.014872000	F	1.109815000	-0.209285000	0.000000000
HOOCl	Total Energy (M06-2X/aug-cc-pVTZ) =-611.09127427				Total Energy (M06-2X/aug-cc-pVTZ) =-611.100034706				Total Energy (M06-2X/aug-cc-pVTZ) =-611.093795228			
	O	-1.512691000	-0.280983000	0.000000000	O	-1.455431000	-0.325767000	-0.121974000	O	0.584183000	-1.333534000	0.000000000
	H	-1.042452000	-1.134494000	-0.000001000	H	-1.615046000	-0.548712000	0.811162000	H	0.139185000	-2.192682000	0.000000000
	O	-0.456008000	0.686046000	0.000000000	O	-0.470475000	0.665708000	0.023354000	O	-0.601581000	-0.524397000	0.000000000
	Cl	0.987767000	-0.123883000	0.000000000	Cl	1.001312000	-0.127695000	-0.001306000	Cl	0.000000000	1.003302000	0.000000000
HOOBr	Total Energy (M06-2X/aug-cc-pVTZ) =-2725.136689391				Total Energy (M06-2X/aug-cc-pVTZ) =-2725.146016601				Total Energy (M06-2X/aug-cc-pVTZ) =-2725.140348337			
	O	-0.467355000	-1.920353000	0.000000000	O	-1.892028000	-0.359410000	-0.122301000	O	0.589884000	-1.774850000	0.000000000
	H	-1.262731000	-1.360005000	0.000000000	H	-2.044345000	-0.597973000	0.808429000	H	0.169045000	-2.647686000	0.000000000
	O	0.625197000	-0.991782000	0.000000000	O	-0.960041000	0.683214000	0.023888000	O	-0.611015000	-0.982938000	0.000000000
	Br	0.000000000	0.704488000	0.000000000	Br	0.710311000	-0.056927000	-0.000604000	Br	0.000000000	0.706000000	0.000000000
$HOOCH_3$	Total Energy (M06-2X/aug-cc-pVTZ) =-190.843035043				Total Energy (M06-2X/aug-cc-pVTZ) =-190.851449485				Total Energy (M06-2X/aug-cc-pVTZ) =-190.851087032			
	O	1.227598000	0.167610000	0.000000000	O	-1.134185000	-0.287522000	-0.094695000	O	1.097425000	-0.342731000	-0.000086000
	H	0.916895000	1.087253000	-0.000001000	H	-1.615607000	-0.043177000	0.708435000	H	1.854244000	0.258130000	0.000178000
	O	0.029209000	-0.619343000	0.000001000	O	-0.029900000	0.617693000	-0.023554000	O	0.032121000	0.620553000	0.000316000
	C	-1.115102000	0.218067000	0.000000000	C	1.117820000	-0.223262000	0.025274000	C	-1.115421000	-0.210884000	-0.000051000
	H	-1.160751000	0.843800000	-0.898629000	H	1.032683000	-0.991222000	-0.741902000	H	-1.121346000	-0.827440000	0.899992000
	H	-1.959240000	-0.469393000	-0.000001000	H	1.967933000	0.423730000	-0.179621000	H	-1.972042000	0.457610000	-0.015105000
	H	-1.160752000	0.843799000	0.898630000	H	1.220748000	-0.691122000	1.007432000	H	-1.104691000	-0.845575000	-0.886600000
$HOOC(CH_3)_3$	Total Energy (M06-2X/aug-cc-pVTZ) =-308.77792021				Total Energy (M06-2X/aug-cc-pVTZ) =-308.788729081				Total Energy (M06-2X/aug-cc-pVTZ) =-308.787524337			
	O	2.054510000	-0.183464000	-0.000711000	O	1.921604000	0.020396000	-0.137301000	O	-1.888718000	-0.000337000	-0.087125000
	H	1.838292000	0.760746000	0.005607000	H	2.332480000	-0.820371000	-0.375771000	H	-2.561091000	0.000096000	-0.778476000
	O	0.788027000	-0.856335000	-0.005620000	O	0.721115000	-0.046131000	-0.910266000	O	-0.709686000	0.000139000	-0.913403000
	C	-0.369521000	0.021492000	-0.000021000	C	-0.386646000	0.020428000	0.030420000	C	0.388466000	-0.000456000	0.030597000
	C	-1.476757000	-1.022596000	-0.007394000	C	-1.608310000	-0.056230000	-0.871972000	C	1.627577000	0.000051000	-0.849372000
	H	-1.381245000	-1.659160000	0.871085000	H	-1.671709000	-1.030766000	-1.353084000	H	1.653677000	0.886367000	-1.482523000
	H	-2.452439000	-0.540920000	0.001033000	H	-2.506292000	0.096357000	-0.274237000	H	2.511195000	0.003866000	-0.211956000
	H	-1.387560000	-1.640664000	-0.899630000	H	-1.567298000	0.715829000	-1.640660000	H	1.658344000	-0.888566000	-1.479601000
	C	-0.445704000	0.900575000	-1.249273000	C	-0.267917000	1.334404000	0.782892000	C	0.308070000	-1.269014000	0.869659000
	H	0.235370000	1.753750000	-1.212020000	H	0.620222000	1.315442000	1.412601000	H	-0.615947000	-1.290831000	1.442827000

	H	-0.239600000	0.321416000	-2.146619000	H	-0.169829000	2.152562000	0.070867000	H	0.333479000	-2.141546000	0.216314000
	H	-1.454334000	1.311681000	-1.325648000	H	-1.141081000	1.502119000	1.411235000	H	1.150900000	-1.318153000	1.558257000
	C	-0.447202000	0.882341000	1.261349000	C	-0.379783000	-1.180385000	0.973739000	C	0.307669000	1.269167000	0.869434000
	H	-1.447791000	1.314785000	1.327199000	H	-1.229624000	-1.104949000	1.654854000	H	1.141926000	1.312422000	1.568904000
	H	-0.269075000	0.285401000	2.153003000	H	-0.481774000	-2.110286000	0.413000000	H	0.347057000	2.141707000	0.217428000
	H	0.253187000	1.720485000	1.248673000	H	0.529095000	-1.219358000	1.571257000	H	-0.623000000	1.297739000	1.431141000
$HOOCF_3$	Total Energy (M06-2X/aug-cc-pVTZ) =-488.631258695				Total Energy (M06-2X/aug-cc-pVTZ) =-488.639985487				Total Energy (M06-2X/aug-cc-pVTZ) =-488.636820458			
	O	1.622791000	-0.994487000	0.000000000	O	1.816256000	-0.004579000	0.117279000	O	-1.781019000	-0.105126000	-0.000596000
	H	0.854989000	-1.597377000	0.000000000	H	2.102915000	-0.142984000	-0.799771000	H	-2.519923000	0.514313000	0.002152000
	O	1.065457000	0.319809000	0.000000000	O	0.709416000	0.860883000	-0.087567000	O	-0.712534000	0.847838000	0.004122000
	C	-0.292773000	0.236045000	0.000000000	C	-0.372334000	0.020231000	0.003454000	C	0.376223000	0.021110000	0.000477000
	F	-0.763124000	1.444477000	0.000000000	F	-1.445624000	0.757957000	-0.001691000	F	1.439324000	0.776072000	-0.007055000
	F	-0.763124000	-0.412320000	-1.052224000	F	-0.428135000	-0.807077000	-1.025276000	F	0.408346000	-0.751509000	1.059475000
	F	-0.763124000	-0.412320000	1.052224000	F	-0.356717000	-0.709639000	1.087117000	F	0.397998000	-0.755970000	-1.056111000

Cartesians coordinates for molecules 1-7 and total energy (in atomic units) from the minimization (Tables S7-S9) obtained at M06-2X/aug-cc-pVTZ level and using the software Gaussian 09:

HOOH				HOOF				HOOCl			
Free Energy (M06-2X/aug-cc-pVTZ) = -151.548119 Enthalpy (M06-2X/aug-cc-pVTZ) = -151.522354				Free Energy (M06-2X/aug-cc-pVTZ) = -250.696462 Enthalpy (M06-2X/aug-cc-pVTZ) = -250.667645				Free Energy (M06-2X/aug-cc-pVTZ) = -611.108914 Enthalpy (M06-2X/aug-cc-pVTZ) = -611.078742			
O	0.000000000000	0.711682000000	-0.058094000000	O	-1.087168000000	-0.227688000000	-0.123721000000	O	-1.491788000000	-0.308593000000	-0.122994000000
H	0.786655000000	0.903492000000	0.464752000000	H	-1.263534000000	-0.551932000000	0.772771000000	H	-1.661115000000	-0.585143000000	0.789205000000
O	0.000000000000	-0.711682000000	-0.058094000000	O	-0.011817000000	0.590017000000	0.037869000000	O	-0.480834000000	0.646066000000	0.029590000000
H	-0.786655000000	-0.903492000000	0.464752000000	F	1.117269000000	-0.260744000000	-0.009551000000	Cl	1.026005000000	-0.124391000000	-0.002469000000
HOOBr				$HOOCH_3$				$HOOC(CH_3)_3$			
Free Energy (M06-2X/aug-cc-pVTZ) = -2725.155996 Enthalpy (M06-2X/aug-cc-pVTZ) = -2725.124517				Free Energy (M06-2X/aug-cc-pVTZ) = -190.822027 Enthalpy (M06-2X/aug-cc-pVTZ) = -190.791404				Free Energy (M06-2X/aug-cc-pVTZ) = -308.681108 Enthalpy (M06-2X/aug-cc-pVTZ) = -308.641446			
O	-1.924889000000	-0.344578000000	-0.122415000000	O	-1.148516000000	-0.267025000000	-0.102788000000	O	-1.943512000000	-0.107227000000	-0.153233000000
H	-2.106246000000	-0.600217000000	0.793150000000	H	-1.573073000000	-0.118731000000	0.750475000000	H	-2.314691000000	0.779625000000	-0.224091000000
O	-0.967487000000	0.665545000000	0.025818000000	O	-0.025364000000	0.601945000000	-0.017419000000	O	-0.730462000000	0.032717000000	-0.882889000000
Br	0.721293000000	-0.056215000000	-0.000582000000	C	1.118140000000	-0.221810000000	0.020838000000	C	0.379807000000	0.000465000000	0.030703000000
				H	1.962964000000	0.465089000000	0.019969000000	C	1.571961000000	0.124229000000	-0.905128000000
				H	1.133687000000	-0.831783000000	0.926250000000	H	1.530252000000	1.063210000000	-1.456107000000
				H	1.158626000000	-0.863070000000	-0.860062000000	H	2.495009000000	0.097808000000	-0.327096000000
								H	1.580251000000	-0.700257000000	-1.616813000000
								C	0.310132000000	1.181251000000	0.988103000000
								H	1.205362000000	1.208798000000	1.609156000000
								H	0.248728000000	2.116835000000	0.430685000000
								H	-0.554481000000	1.098278000000	1.645050000000
								C	0.400562000000	-1.324615000000	0.776961000000
								H	0.430167000000	-2.152707000000	0.069415000000
								H	1.282631000000	-1.376461000000	1.415603000000
								H	-0.486203000000	-1.427020000000	1.399332000000

$HOOCF_3$			Radical OH			Radical OF		
Free Energy (M06-2X/aug-cc-pVTZ) = -488.637697			Free Energy (M06-2X/aug-cc-pVTZ) = -75.74218			Free Energy (M06-2X/aug-cc-pVTZ) = -174.897259		
Enthalpy (M06-2X/aug-cc-pVTZ) = -488.602268			Enthalpy (M06-2X/aug-cc-pVTZ) = -75.721954			Enthalpy (M06-2X/aug-cc-pVTZ) = -174.873309		
O	-1.856092000000	0.002734000000	0.120459000000	O	0.000000000000	0.000000000000	0.107999000000	O	0.000000000000	0.000000000000	-0.703304000000
H	-2.145384000000	0.049238000000	-0.801526000000	H	0.000000000000	0.000000000000	-0.863995000000	F	0.000000000000	0.000000000000	0.625159000000
O	-0.715287000000	-0.827076000000	0.023679000000								
C	0.380960000000	-0.009080000000	0.002872000000								
F	1.428154000000	-0.807642000000	-0.068133000000								
F	0.370577000000	0.795909000000	-1.056979000000								
F	0.471343000000	0.745065000000	1.084133000000								
Radical OCl			Radical OBr			Radical OCH_3		
Free Energy (M06-2X/aug-cc-pVTZ) = -535.326929			Free Energy (M06-2X/aug-cc-pVTZ) = -2649.371708			Free Energy (M06-2X/aug-cc-pVTZ) = -115.02876		
Enthalpy (M06-2X/aug-cc-pVTZ) = -535.301869			Enthalpy (M06-2X/aug-cc-pVTZ) = -2649.345384			Enthalpy (M06-2X/aug-cc-pVTZ) = -115.001493		
O	0.000000000000	0.000000000000	-1.066316000000	O	0.000000000000	0.000000000000	-1.392606000000	O	0.791578000000	0.005110000000	-0.000013000000
Cl	0.000000000000	0.000000000000	0.501796000000	Br	0.000000000000	0.000000000000	0.318310000000	C	-0.577225000000	0.011165000000	-0.000084000000
								H	-1.018050000000	1.011836000000	-0.002338000000
								H	-0.925687000000	-0.562153000000	-0.871114000000
								H	-0.925538000000	-0.557549000000	0.874053000000
Radical $OC(CH_3)_3$			Radical OCF_3					
Free Energy (M06-2X/aug-cc-pVTZ) = -232.885292			Free Energy (M06-2X/aug-cc-pVTZ) = -412.832775					
Enthalpy (M06-2X/aug-cc-pVTZ) = -232.848677			Enthalpy (M06-2X/aug-cc-pVTZ) = -412.79949					
O	0.001692000000	-0.263560000000	1.427181000000	O	-0.785606000000	-0.011642000000	1.147947000000				
C	-0.000190000000	0.023663000000	0.076131000000	C	-0.006648000000	-0.000170000000	0.033180000000				
C	-1.270581000000	0.778629000000	-0.311781000000	F	0.773708000000	-1.068474000000	-0.032428000000				
H	-2.149633000000	0.202044000000	-0.027932000000	F	0.770148000000	1.071251000000	-0.014105000000				
H	-1.304701000000	1.739706000000	0.200914000000	F	-0.841108000000	0.007685000000	-0.995985000000				
H	-1.294695000000	0.960582000000	-1.386496000000								
C	0.009399000000	-1.374270000000	-0.578993000000								
H	-0.874378000000	-1.937312000000	-0.285713000000								
H	0.007809000000	-1.240597000000	-1.660612000000								
H	0.901534000000	-1.924545000000	-0.286799000000								
C	1.259906000000	0.795716000000	-0.311646000000								
H	2.146635000000	0.230897000000	-0.028012000000								
H	1.281501000000	0.978227000000	-1.386318000000								
H	1.281190000000	1.757051000000	0.201252000000								