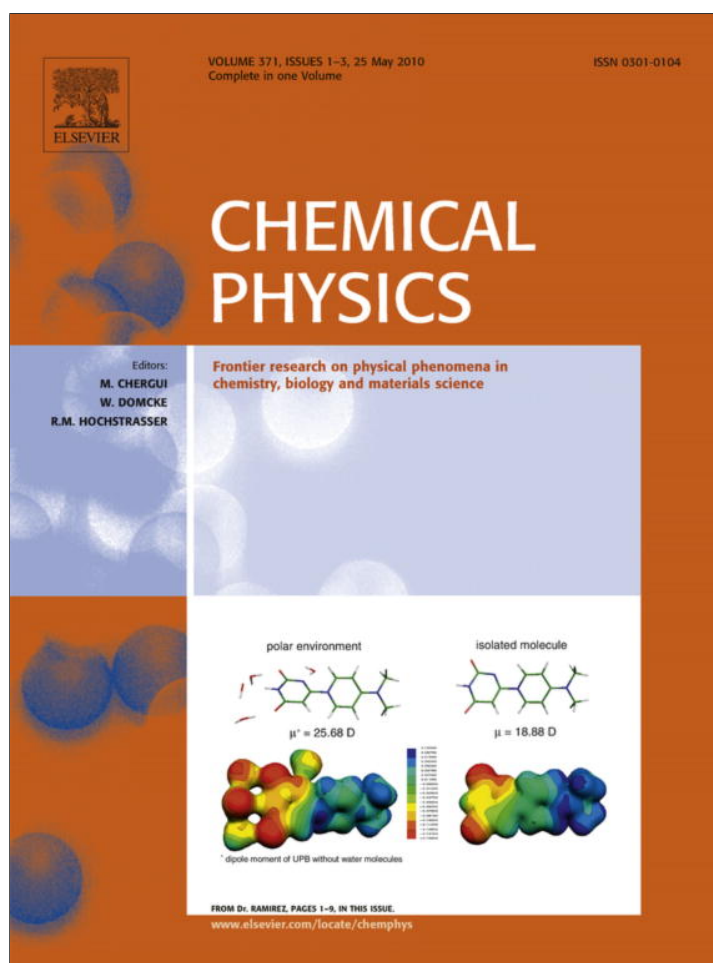


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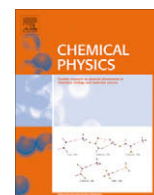
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Structural and heat of formation studies of halogenated methyl hydro-peroxides

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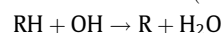
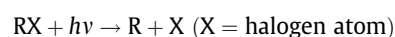
ABSTRACT

The computational characterization of a series of halomethyl hydro-peroxides, $\text{CH}_n\text{X}_{3-n}\text{OOH}$ and the halomethyl haloperoxide isomeric structures, $\text{CH}_{n+1}\text{X}_{2-n}\text{OOX}$, ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$), is carried out using density functional theory techniques and ab initio electronic structure methods. The results show a considerable thermodynamic stability for some of these compounds and interesting structural trends and energy variations among the hydro-peroxides and between the hydro-peroxides and the haloperoxide isomers. The significant differences obtained in the relative stabilities and the heat of formation values for $\text{X} = \text{F}$ to $\text{X} = \text{I}$ and $\text{X} = \text{H}$, are discussed in terms of the induction effect of the halogen atoms present in the methylic group and the relative strength of the terminal O–X bond, $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{H}$, in correlation with the order of decreasing electronegativity.

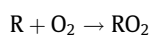
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1. Introduction

Alkyl hydro-peroxides, ROOH, are interesting intermediates in the atmospheric oxidation and combustion of simple and halogenated hydrocarbons [1–3]. The chain reactions that take place in these processes, initiated via either photodissociation of a light halogenated hydrocarbon or attack by a hydroxyl radical, yield alkyl radicals



which can readily pick up an oxygen molecule



The alkylperoxy radicals formed, present a rich chemistry and give self-reactions or react with other active species producing a variety of oxidized products [2,4–8]. In low concentrations of NO_x , the most important reactions involve the abundant hydroperoxy radicals [2,9] leading to the production of ROOH



The alkyl hydro-peroxides are relatively stable adducts under atmospheric conditions that are removed from the troposphere via precipitation [5]. Knowledge of their structure and thermodynamics is useful for studying the mechanism of the oxidation pathways in the chemistry of combustion and flames, in atmospheric chemistry and in various biochemical oxidizing processes. Hence, several experimental and theoretical investigations have been carried out to

examine and characterize the geometrical, spectroscopic and thermochemical properties of simple and halogenated alkyl hydro-peroxides [10–22].

Most studies on organic hydro-peroxides have been devoted to the simplest member of the series, i.e., methyl hydroperoxide, CH_3OOH , extending eventually to other alkyl derivatives, ROOH. Focus in several reports has been given on changing the size and the branching of the alkyl group along the sequence $\text{R} = \text{methyl}, \text{ethyl}, \text{isopropyl}, \text{tert-butyl}, \text{isobutyl}$ and sec-butyl [22] in order to determine the effect of increased aliphatic chain and branching on bond energies and thermodynamic stability. Less attention has been given to examine the induction effect of halogen substitution in the alkyl group. Among these latter studies, Knyazev et al. [17] using experimentally determined parameters and Sun et al. [18] theoretically, have investigated the effect of successive chlorination on CH_3OOH . El-Taher [21] has examined several fluorinated methyl hydro-peroxides. The main tendency that is quoted in these reports is that halogenation of the methyl group affects favorably the thermodynamic stability of the resulting species.

In the present work the computational characterization of several members of the family of halogenated methyl hydro-peroxides, $\text{CH}_n\text{X}_{3-n}\text{OOH}$ and their halomethyl haloperoxide isomers, $\text{CH}_{n+1}\text{X}_{2-n}\text{OOX}$, ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) is carried out using density functional theory techniques and ab initio electronic structure methods. The equilibrium geometries and the thermodynamic stabilities of the hydro-peroxides are determined and the structural variations among them and the isomeric haloperoxides are investigated. The decreasing ΔH_f tendencies observed for the fluorinated species are not followed monotonously for the heavier halogenated compounds. Significant differences are also observed in the relative stabilities and the heat of formation results of the

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isomeric species, depending on the halogen atoms present in the methylic group.

2. Computational details

The geometry optimizations and frequency calculations have been performed at the MP2/6-31G(d) [23,24] and the B3LYP/6-311++G(d,p) [25,26] levels of theory, for all species except the iodinated compounds. The energetics have been further refined by employing single point couple-cluster CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p) calculations [27,28]. The optimization of the iodinated compounds has also been carried out at the MP2 level of theory but using the LANL2DZ basis set which is based on the Hay-Wadt relativistic effective core potential [29]. For the purpose of the present computations the standard LANL2DZ basis set has been augmented with a set of uncontracted *s* and *p* diffuse functions (exponents 0.0569 and 0.0330, respectively) and *d* and *f* polarization functions (exponents 0.292 and 0.441, respectively) [30,31] and it is denoted hereafter as LANL2DZspdf [32,33]. The remaining atoms, C, O and H in the I containing compounds have been treated with the standard 6-311++G(d,p) basis set. All calculations have been carried out with the use of the Gaussian 03 series of programs [34].

The $\text{CH}_n\text{X}_{3-n}\text{-OOH}$ bond dissociation energies (BDE) have been evaluated from the calculated reaction energy ΔE_r of the dissociation channel into $\text{CH}_n\text{X}_{3-n} + \text{HO}_2$. The heat of formation values, ΔH_f° at 298 K for the hydro-peroxides have also been obtained from the same dissociation channel using the reaction energy, ΔE_r , as applied by other workers [35], including thermal corrections. The fluorobromomethyl hydroperoxide for which no reported data of the corresponding CHBr radical exist, has been treated using G2MP2 computational thermochemistry protocol [36] by following the procedure based on atomization energies, as outlined by Curtiss et al. [37]. Tabulated data [38] and recently reported thermochem-

ical data [39–41] have been used for the halogenated alkyl groups and are collected in Table 4. The value $\Delta H_f^\circ = 3.9 \text{ kcal mol}^{-1}$ at 298 K has been employed for HO_2 [42]. More recent is the value $2.94 \pm 0.06 \text{ kcal mol}^{-1}$ obtained by Ruscic et al. [46] leading to ΔH_f° (298) calculated results differing by about 1 kcal mol^{-1} .

3. Structural and frequency results

The most important structural data are summarized in Tables 1 and 2 (MP2 and B3LYP levels, respectively). Table 3 contains the torsional frequencies, i.e., the CX_3 twist around the C–O bond and the internal rotation around the peroxide O–O bond. Tables 4 and 5 summarize the energetics and the thermodynamical results while example structures of some hydro-peroxides and their isomers are depicted in Fig. 1. Inspection of Tables 1 and 2 indicates a good overall consistency between the MP2 and B3LYP optimizations. Despite small or occasionally, significant differences in the results of the two methodologies, both series of calculations exhibit exactly the same tendencies and trends and emphasize similar phenomena and intramolecular interactions. Inclusion of the structural data of the well studied methyl hydroperoxide allows also an interesting comparison with the maternal species.

The main feature observed in Tables 1 and 2 is the significant decrease of the C–O bond distance in all halogenated hydro-peroxides, $\text{CH}_n\text{X}_{3-n}\text{OOH}$, compared to CH_3OOH , a direct consequence of the halogen induction effect that strongly polarizes the X–C bond compared to H–C. However, no clear halogen dependence is evident but rather a comparable more or less reduction of the C–O length, independent of the number and the specific halogen atoms present in the methylic fragment. El-Taher [21] quotes a correlation between the successive fluorination and the progressive tightening of the C–O bond, analogous to the effect of successive chlorination observed by Bozzelli et al. [18]. This trend though, is actually true only for the first two members, CH_2XOOH and

Table 1
Most important structural parameters (\AA , $^\circ$) at the MP2/6-31G(d) level of theory.^a

	C–O	C–F	C–Cl	C–Br	C–I	O–O	O–H	O–X	ϕ^b
CH_3OOH	1.419 (1.4188)	–	–	–	–	1.462	0.971	–	118.1
CH_2FOOH	1.368 (1.3857)	1.385	–	–	–	1.464	0.978	–	91.1
CH_3OOF	1.438	–	–	–	–	1.383	–	1.479	80.7
CHF_2OOH	1.389 (1.3541)	1.348	–	–	–	1.468	0.978	–	97.1
CH_2FOOF	1.409	1.369	–	–	–	1.404	–	1.464	81.7
CF_3OOH	1.378 (1.3776)	1.333	–	–	–	1.458	0.979	–	103.0
CHF_2OOF	1.413	1.340	–	–	–	1.401	–	1.465	85.8
CH_2ClOOH	1.390	–	1.792	–	–	1.461	0.972	–	98.4
CH_3OOCI^c	1.421	–	–	–	–	1.405	–	1.761	88.0
CHClFOOH	1.377	1.354	1.780	–	–	1.460	0.980	–	104.3
CH_2ClOOF	1.417	–	1.769	–	–	1.399	–	1.470	80.5
CH_2FOOCl	1.397	1.371	–	–	–	1.453	–	1.734	95.2
CCl_2FOOH	1.389	1.346	1.774	–	–	1.454	0.980	–	103.6
CHClFOOCl	1.399	1.358	1.765	–	–	1.450	–	1.724	100.8
CHCl_2OOF	1.411	–	1.760	–	–	1.371	–	1.455	97.2
CH_2BrOOH	1.395	–	–	1.936	–	1.476	0.978	–	109.8
CH_3OObR	1.429	–	–	–	–	1.435	–	1.906	85.8
CHBrOOH	1.373	1.367	–	1.949	–	1.461	–	–	89.5
CH_2FOObR	1.431	1.363	–	–	–	1.437	–	1.905	89.4
CH_2BrOOF	1.402	–	–	1.947	–	1.400	–	1.467	79.5
CHClBrOOH	1.381	–	1.776	1.950	–	1.459	0.980	–	100.9
CH_2ClOObR	1.430	–	1.756	–	–	1.444	–	1.902	88.4
CH_2BrOOCl	1.400	–	–	1.953	–	1.451	–	1.736	89.4
CH_2IOOH^d	1.384	–	–	–	2.161	1.437	0.967	–	101.2
CH_3OOI^d	1.418	–	–	–	–	1.438	–	2.005	89.6
CHI_2OOH^d	1.378	–	–	–	2.155	1.440	0.968	–	101.9
CH_2IOOI^d	1.413	–	–	–	2.111	1.448	–	2.001	96.2

^a Data in parentheses from Ref. [21].

^b ϕ denotes the dihedral angle COOX, X = H, F, Cl, Br, I.

^c Ref. [45].

^d At the MP2/LANL2DZspdf level, see text for details.

Table 2
Most important structural parameters (Å, °) at the B3LYP/6-311++G(d,p) level of theory.^a

	C–O	C–F	C–Cl	C–Br	O–O	O–H	O–X	ϕ^b
CH ₃ OOH	1.421 (1.4168)	–	–	–	1.450	0.972	–	112.1
CH ₂ FOOH	1.378 (1.3832)	1.394	–	–	1.454	0.969	–	73.1
CH ₃ OOF	1.448	–	–	–	1.343	–	1.519	82.8
CHF ₂ OOH	1.389 (1.3752)	1.351	–	–	1.468	0.978	–	70.7
CH ₂ FOOF	1.415	1.370	–	–	1.376	–	1.469	87.1
CF ₃ OOH	1.375 (1.3778)	1.334	–	–	1.445	0.970	–	98.8
CHF ₂ OOF	1.413	1.336	–	–	1.366	–	1.465	86.9
CH ₂ CIOOH	1.377	–	1.842	–	1.449	0.974	–	95.2
CH ₃ OOCI	1.428	–	–	–	1.411	–	1.782	89.1
CHClFOOH	1.369	1.368	1.795	–	1.449	0.970	–	100.0
CH ₂ CIOF	1.417	–	1.794	–	1.365	–	1.487	73.9
CH ₂ FOOCl	1.407	1.376	–	–	1.421	–	1.767	72.0
CCl ₂ FOOH	1.381	1.339	1.806	–	1.437	0.971	–	104.8
CHClFOOCl	1.404	1.356	1.792	–	1.438	–	1.744	72.9
CHCl ₂ OOF	1.415	–	1.782	–	1.379	–	1.462	96.1
CH ₂ BrOOH	1.399	–	–	1.954	1.461	0.968	–	117.7
CH ₃ OObR	1.431	–	–	–	1.394	–	1.960	85.9
CHBrOOH	1.365	1.367	–	1.972	1.449	–	–	99.9
CH ₂ FOObR	1.433	1.361	–	–	1.391	–	1.945	90.8
CH ₂ BrOOF	1.419	–	–	1.962	1.363	–	1.488	81.2
CHClBrOOH	1.367	–	1.809	1.973	1.446	0.971	–	104.1
CH ₂ CIOObR	1.432	–	1.777	–	1.399	–	1.936	89.5
CH ₂ BrOOCl	1.402	–	–	1.987	1.427	–	1.756	108.3

^a Data in parentheses from Ref. [21].

^b ϕ denotes the dihedral angle COOX, X = H, F, Cl, Br, I.

Table 3
Torsional frequencies (cm⁻¹) at the MP2/6-31G(d) (first column) and B3LYP/6-311++G(d,p) (second column) levels of theory ν_1 for the CX₃ twist around the C–O bond and ν_2 for the internal rotation around the peroxide O–O bond.

	ν_1 (CX ₃ twist)		ν_2 (O–O)		ν_1 (CX ₃ twist) ν_2 (O–O)				
CH ₃ OOH	267	254	164	168					
CH ₂ FOOH	165	168	290	262	CH ₂ BrOOH	104	112	232	229
CH ₃ OOF	211	193	163	147	CH ₃ OObR	221	188	139	134
CHF ₂ OOH	125	109	238	230	CH ₂ IIOOH	134	–	228	–
CH ₂ FOOF	178	163	97	107	CH ₃ OObI	202	–	115	–
CF ₃ OOH	150	137	262	248	CHCl ₂ OOH	120	–	193	–
CHF ₂ OOF	142	141	71	64	CH ₂ IIOOI	94	–	43	–
CH ₂ CIOOH	163	155	274	255					
CH ₃ OOCI	218	195	135	131					
CHClFOOH	161	145	254	231	CHBrOOH	153	133	224	207
CH ₂ CIOF	179	170	81	70	CH ₂ FOObR	134	117	62	34
CH ₂ FOOCl	154	158	73	69	CH ₂ BrOOF	175	164	73	61
CCl ₂ FOOH	145	130	228	218	CHClBrOOH	147	127	218	203
CHClFOOCl	108	95	73	76	CH ₂ CIOObR	129	114	60	43
CHCl ₂ OOF	145	131	72	84	CH ₂ BrOOCl	137	115	52	68

CHX₂OOH, X = F, Cl while the C–O bond length in CF₃OOH and CCl₃OOH was reported to increase again (Table 1). Interestingly enough, no C–O bond variation is observed in the halomethyl haloperoxides which result from the substitution of H atoms by halogens in the CH₃ fragment. The C–O bond distances in R'OOX (R' = CH_{n+1}X_{2-n}) range more or less around the C–O value of the maternal methyl hydroperoxide and no differentiation towards a particular direction is apparent.

The peroxide O–O bond distance is the other structural parameter with an interesting behavior. It shows negligible changes among the hydro-peroxides assuming similar values as in CH₃OOH or just slightly larger, while it shows strong fluctuations in the haloperoxides. First a severe decrease is obtained in the fluoroperoxides which present quite small O–O bond distances tending to the free molecular oxygen bond distance, 1.208 Å. In R'OOCI and R'OObR, the O–O bond length assumes moderately smaller values than O–O in the corresponding hydro-peroxides but not as short as in the R'OOF cases. Finally, the iodoperoxides break this trend and display O–O bond distances comparable between the hydro-

peroxide and the iodoperoxide isomers. Consequently, the O–O bond distance variation shows a strong dependence on the X atom of the O–X bond, X = H, F, Cl, Br, I, relating apparently with the electronegativity of X. The very high electronegativity of F makes the O–F bond to be the weakest of all O–X bonds and via intramolecular interaction, causes a severe shortening of the peroxide CO–O–F bond. Chlorine and bromine derivatives show milder consequences of this effect since Cl and Br can hold partial positive charges in the O–Cl and O–Br bonds opposite to the partial charge distribution in R'OOF. The iodoperoxides show comparable O–O distances as iodomethyl hydro-peroxides, due to the similar, much lower electronegativities of I and H. These regularities indicate that the halogen induction effect in the methyl group is not the sole factor that influences the geometry of the equilibrium state. The geometrical features are equally affected by both the halogenation of the methyl group and the electronegativity of X in the O–X bond, X = H, F, Cl, Br, I.

The remaining structural parameters are modified by the same phenomena but to a lesser degree. The C–F bond distance in most

Table 4

R–OOH bond dissociation energies (BDE) and heat of formation values, ΔH_f° at 298 K for several halogenated methyl hydro-peroxides and reported ΔH_f° values for the fragments R and HO₂ (kcal mol⁻¹).

	Present results ^a BDE	ΔH_f° (298)	Ref. [21]	Ref. [18]	Exp.
CH ₃ OOH	65.4, 61.0 ^b	-31.8	-32.3	-31.6	-33.2 ± 1.9 ^d
CH ₂ FOOH	72.9, 69.9 ^b	-82.5	-83.9	-	-
CHF ₂ OOH	74.8, 71.6 ^b	-136.9	-138.3	-	-
CF ₃ OOH	75.8, 72.2 ^b	-191.9	-192.4	-	-191.0 ± 5 ^b
CHClFOOH	70.9	-82.2	-	-	-
CCl ₂ FOOH	67.3	-92.5	-91.0	-	-
CH ₂ ClOOH	71.8, 72.9 ^c	-40.8	-	-41.41 ± 1.45 ^c	-36.6 ± 4 ^e
CHCl ₂ OOH	-	-	-	-44.74 ± 3.25 ^c	-40.0 ± 3.4 ^e
CCl ₃ OOH	-	-	-	-45.63 ± 3.14 ^c	-
CHBrOOH	70.4	-78.0 ^k	-	-	-
CHClBrOOH	63.6	-36.2	-	-	-
CH ₂ BrOOH	61.2	-27.4	-	-	-
CH ₂ IOOH ^f	113.8	-58.1, -55.4	-	-	-
CHI ₂ OOH ^f	109.8	-36.5, -30.8	-	-	-
ΔH_f° (298) reported values for the alkyl radicals					
CH ₃ ^d	35.0	CHClF ^j	-15.2	CHClBr	31.1 ^k , 34.7 ^d
CH ₂ ^{fj}	-6.9	CCl ₂ ^{fj}	-22.5	CH ₂ Br ^l	39.8
CHF ₂ ^j	-57.6	CH ₂ Cl ^l	27.9	CH ₂ I	51.9 ^l , 54.5 ± 0.7 ^m
CF ₃ ^j	-111.3	CHBr ^k	-6.3	CHI ₂	69.4 ^l , 75.1 ± 0.8 ^m

^a CCSD(T)//B3LYP calculations and ΔH_f° (298) based on ΔH_f° (298) of HO₂ = 3.9 kcal mol⁻¹ [42]. Ruscic's ΔH_f° (298) of HO₂ = 2.94 ± 0.06 kcal mol⁻¹ [46] leads to results lower by about 1 kcal mol⁻¹.

^b Ref. [21].

^c Ref. [18].

^d Ref. [38].

^e Ref. [17].

^f Two results based on two reported values for ΔH_f° (298) of CH₂I, CHI₂, Refs. [40,41].

^j Ref. [39].

^k Based on atomization energy calculations.

^l Ref. [40].

^m Ref. [41].

Table 5

Electronic energies, E_H (Hartrees) and relative energies including ZPE corrections, ΔE , and heat of formation, ΔH_f° at 298 (kcal mol⁻¹).

	MP2/6-31G(d)		B3LYP/6-311++G(d,p)		CCSD(T)//B3LYP		
	E_H	ΔE	E_H	ΔE	E_H	ΔE	ΔH_f°
CH ₂ FOOH	-289.23182	0.0	-290.10034	0.0	-289.50871	0.0	-82.5
CH ₃ OOF	-289.12074	69.7	-289.99284	67.5	-289.39346	72.3	-10.2
CHF ₂ OOH	-388.28177	0.0	-389.38915	0.0	-388.60365	0.0	-136.9
CH ₂ FOOF	-388.15898	77.1	-389.27328	72.7	-388.48034	77.4	-59.5
CF ₃ OOH	-487.34152	0.0	-488.68388	0.0	-487.70518	0.0	-191.9
CHF ₂ OOF	-487.20940	82.9	-488.56389	75.3	-487.57676	80.6	-111.3
CH ₂ ClOOH	-649.45625	0.0	-650.48428	0.0	-649.65132	0.0	-40.8
CH ₃ OOC ^b	-649.39713 ^b	37.1	-650.42563	36.8	-649.59108	37.8	-3.0
CHClFOOH	-748.29037	0.0	-749.73882	0.0	-748.57967	0.0	-82.2
CH ₂ ClOOF	-748.17409	73.0	-749.62912	68.8	-748.46751	70.4	-11.8
CH ₂ FOCl	-748.22906	38.6	-749.67766	38.4	-748.51552	40.3	-41.9
CCl ₂ FOOH	-1207.34239	0.0	-1209.36958	0.0	-1207.65232	0.0	-92.5
CHCl ₂ OOF	-1207.22598	73.0	-1209.25858	69.7	-1207.53489	73.7	-18.8
CHClFOCl	-1207.28678	34.9	-1209.31432	34.7	-1207.59015	39.0	-53.5
CH ₂ BrOOH	-2759.70308	0.0	-2764.45165	0.0	-2762.28529	0.0	-27.4
CH ₃ OOb ^r	-2759.70308	25.1	-2764.41174	25.0	-2762.28529	29.6	2.2
CHBrOOH	-2858.69766	0.0	-2863.65955	0.0	-2861.42702	0.0	-78.0
CH ₂ FOOb ^r	-2858.64311	34.2	-2863.60701	33.0	-2861.36897	36.4	-41.6
CH ₂ BrOOF	-2858.58443	71.1	-2863.55100	68.1	-2861.31228	72.0	-6.0
CHClBrOOH	-3218.71136	0.0	-3224.00985	0.0	-3221.40926	0.0	-36.2
CH ₂ ClOOb ^r	-3218.66415	29.6	-3223.96369	29.0	-3221.35788	32.2	-4.0
CH ₂ BrOCl	-3218.65477	35.5	-3223.95282	35.8	-3221.34524	40.2	4.0
CH ₂ IOOH	-201.08255	0.0	-	-	-201.13976	0.0	-58.1
CH ₃ OCl	-201.04610	22.9	-	-	-201.10657	20.8	-37.3
CHI ₂ OOH ^a	-211.79916	0.0	-	-	-211.90441	0.0	-36.5
CHI ₂ OCl ^a	-211.76458	21.7	-	-	-211.87419	18.9	-17.6

^a CCSD(T)//MP2/LANL2DZspdf results, see text for details.

^b Ref. [45].

cases decreases upon further introduction of additional halogen atoms into the methyl group while a weak increasing dependence is obtained for the other C–X bond distances in the presence of

other halogens in the methyl group. The dihedral angle results, φ = COOX, are also interesting and generally, the equilibrium structures of all species studied assume a near skew configuration. The

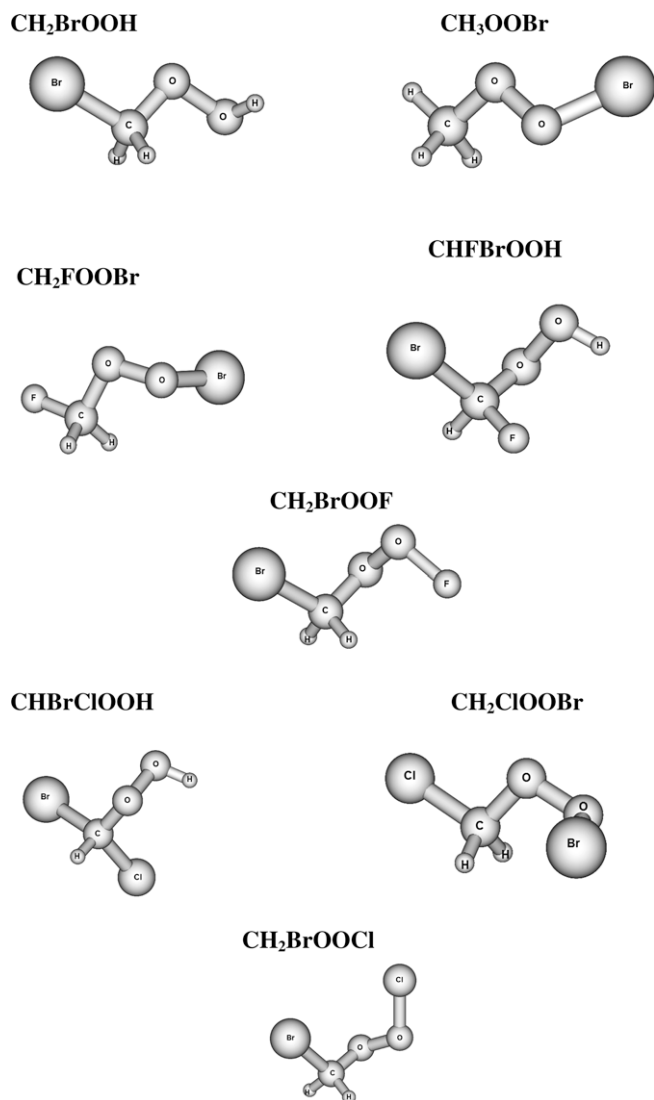


Fig. 1. Sample structures of brominated hydro-peroxides and isomeric forms.

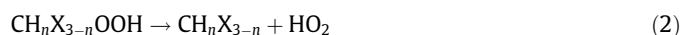
largest φ value is computed at both at MP2 and B3LYP levels for the maternal compound, methyl hydroperoxide, CH_3OOH , where the stereochemical interactions are minimum. The other hydroperoxides follow with smaller φ values but larger than the isomeric haloperoxides at the MP2 level. The B3LYP values are more confused and in a couple of cases, the haloperoxides present larger φ values than the isomeric hydro-peroxides. Fig. 1 contains sample structures of some peroxides (the brominated species) that display the methylic halogen orientation. The examples illustrate clearly that the lowest energy conformations have the peroxy oxygen placed gauche to the maximum number of halogens of the methyl group, despite the apparent steric penalty paid for such a configuration. This is because the gauche orientation of the peroxy group is consistent with a tendency to minimize the repulsion between nonbonding electron pairs of oxygen atom and halogen atom and allows the intramolecular interaction between the peroxy hydrogen in O–H and a halogen atom on the methyl group [18].

Table 3 contains the two torsional frequencies for each system: ν_1 for the CX_3 twist around the C–O bond and ν_2 for the internal rotation around the peroxide bond, with ν_1 about twice ν_2 in CH_3OOH . The calculations indicate clearly the reversing of this order and the abrupt drop of the $\text{CH}_n\text{X}_{3-n}$ torsional frequency ν_1 to about half the value of ν_2 in $\text{CH}_n\text{X}_{3-n}\text{OOH}$, $\nu_1 \sim \nu_2/2$, due to the

redistribution of masses from the introduction of the heavy halogen atoms into the methyl group. In the halomethyl haloperoxides, $\text{CH}_{n+1}\text{X}_{2-n}\text{OOX}$, X = F, Cl, Br, I, the two frequencies recover the opposite trend, $\nu_1 \sim 2\nu_2$ and resemble the tendency followed in the maternal species, CH_3OOH .

4. Energetics and heat of formation results

Table 4 contains the calculated R–OO–H bond dissociation energies (BDE) based on the reaction energy, ΔE_r , of the dissociation reaction, Eq. (2)



Heat of formation values, ΔH_f° at 298, computed from the same reaction energies of Eq. (2), ΔE_r , in which thermal energy corrections have been included, are also collected in Table 4, along with available literature data for the halomethyl radicals, $\text{CH}_n\text{X}_{3-n}$. The recently reported [42] heat of formation value ΔH_f° at 298 for HO_2 , $3.9 \text{ kcal mol}^{-1}$ has been combined. Fluorobromomethyl hydroperoxide, CHFBrOOH , has been an exception in this procedure, due to the lack of thermodynamic data for the fluorobromomethyl radical, CHFBr . In this case, atomization energy methodologies [36,37] have been used for the calculation of the heat of formation at 298 K for both CHFBr and CHFBrOOH and as a test, for the CHClBr radical (Table 4). For the iodomethyl derivatives two ΔH_f° values are calculated based on two ΔH_f° values for CH_2I and CHI_2 radicals, one computed by Marshall et al. [40] and the other determined experimentally by Seetula [41]. Table 5 summarizes the calculated electronic energies, E_H , the relative energies of the haloperoxide isomers with respect to the hydroperoxide compounds, ΔE_{is} , and the calculated ΔH_f° at 298 for all species considered.

The $\text{CH}_n\text{X}_{3-n}\text{OOH}$ bond dissociation energies, $\text{BDE}(\text{R–OOH})$ calculated at the $\text{CCSD(T)}/\text{B3LYP}$ level (Table 4), exhibit a significant dependence on the number and the kind of halogen atoms present in $\text{CH}_n\text{X}_{3-n}$. They vary with the increasing number of fluorine atoms in the fluoromethyl hydro-peroxides compared to CH_3OOH , in good agreement with the reported results [21] and the decreasing tendency of the C–O bond distance. Chlorination also increases the CH_2ClOOH bond dissociation energy compared to CH_3OOH but the presence of additional chlorine [18] and bromine atoms leads to declining $\text{BDE}(\text{R–OOH})$ values, assumingly due to the weaker induction effect of Cl and Br compared to F. The effect of I atoms is interesting since it leads to significantly larger $\text{BDE}(\text{R–OOH})$ results although introduction of the second I atom does have a decreasing effect. Apparently, the influence of the iodine in the methyl group because of its lower electronegativity, rather resembles the effect of the increasing chain and branching of the alkyl fragment [22] than the halogen induction effect. Indeed, EtOOH and iPrOOH have been found to present increasing $\text{BDE}(\text{R–OOH})$ values compared to MeOOH [22].

Table 4 lists the heat of formation, ΔH_f° (298), results which show the good agreement of the present calculations with reported values wherever available. Certainly, the ΔH_f° value is not the proper measure of the thermodynamic stability of a compound, since the kinetic factors severely affect the reactivity. However, we do believe that ΔH_f° which is an important property characterizing a system of atmospheric significance, may to a certain extent give an indication of its thermodynamic stability. The consideration of the ΔH_f° (298) for all species investigated reveals interesting variations among the hydro-peroxides and the haloperoxides. Thus, the fluoromethyl derivatives present the lowest ΔH_f° (298) values among all hydro-peroxides and the same is true for the mixed fluorochloromethyl and bromofluoromethyl species, reflecting the large strength of the C–F bond. The results confirm the general observation that the presence of fluorine atoms in the methyl group leads

to particularly low values of ΔH_f^0 (298) for the fluoromethyl systems [6]. The remaining hydro-peroxides follow a peculiar order of the ΔH_f^0 (298) values. With the exception of bromomethyl hydroperoxide, CH_2BrOOH , they all have lower ΔH_f^0 (298) values than CH_3OOH with the iodomethyl compound having the lowest of all. However, when a second I atom is introduced, ΔH_f^0 (298) increases and the final order of the ΔH_f^0 (298) values becomes: $\text{CH}_2\text{IOOH} < \text{CH}_2\text{ClOOH} < \text{CHClBrOOH} \sim \text{CHI}_2\text{OOH} < \text{CH}_3\text{OOH} < \text{CH}_2\text{-BrOOH}$. The bromomethyl hydroperoxide is found to present the highest ΔH_f^0 (298) value among all species and this observation is in agreement with literature results about the feasibility of Br removal in oxidized bromoalkyl compounds [43,44].

Finally, Table 5 summarizes the relative stabilities, ΔE_{is} , i.e., the isomerization energies of the methyl haloperoxides with respect to the isomeric hydro-peroxides and the overall heat of formation results. The largest ΔE_{is} values are computed for the fluoroperoxides, ROOF, that are found to be the most unstable species in each subfamily. In contrast to the effect of fluorine atoms in the methyl group, which particularly stabilizes the fluoromethyl hydro-peroxides, the shifting of fluorine to the peroxide oxygen to give the ROO–F type connectivity largely destabilizes the resulting structure. The iodoperoxides present the lowest isomerization energies while ROOCl and ROOBr isomers are located between ROOF and ROOI in terms of relative stability. Characteristic examples that demonstrate clearly these tendencies are the CHFClOOH and CHFB-ROOH subfamilies. The hydroperoxide forms present quite low ΔH_f^0 (298) values -82.2 and -78.0 kcal mol $^{-1}$, respectively, due to the presence of the F atom in the methyl group. The CH_2ClOOF and CH_2BrOOF isomers are found to be quite unstable relative to the former by 73.0 and 71.1 kcal mol $^{-1}$, apparently due to the involvement of the unstable O–F bond. The chloro- and bromo-species lie in between with the relative energies of CH_2FOOCl and CH_2FOOBr dropping almost by half to just 38.6 and 34.2 kcal mol $^{-1}$, respectively.

The comparison of the ΔH_f^0 (298) values for all species examined (Table 5) gives an overall picture of the order of the ΔH_f^0 (298) values of the compounds $\text{CX}_n\text{Y}_{3-n}\text{OOX}$ (X, Y = H, F, Cl, Br, I). As already emphasized in the previous paragraph, the lowest ΔH_f^0 (298) values among all species considered, either hydro- or halo-peroxides correspond to those containing fluorine atoms in the methyl group, which all present lower heat of formation values than the maternal methyl peroxide. The second regularity observed are the higher ΔH_f^0 (298) values of all haloperoxides ROOX, X = F, Cl, Br with the exception of the fluoromethyl species and the high ΔH_f^0 (298) values of the brominated species. The latter involving Br either in the methyl group or the peroxy part, may be considered the least stable structures with CH_2BrOOH being the only hydroperoxide with a higher ΔH_f^0 (298) value than CH_3OOH . Finally, the iodinated derivatives display good thermodynamic stability and methyl iodoperoxide exhibits a lower ΔH_f^0 (298) value than CH_3OOH .

5. Summary

We have computationally investigate a series of halomethyl hydro-peroxides and their isomeric halomethyl haloperoxides in order to examine the changes invoked in the geometrical, spectroscopic and energetic parameters, due to the effect of hydrogen substitution by halogen atom either in the methyl group or the hydroxy O–H part. The heat of formation computations performed are also valuable for the atmospheric chemistry of these species, since the thermodynamic parameters affect the reactivity of a system, although they are not the only factor that determines the kinetic behavior. The present results show that both the halogen atom in the methyl group and the halogen atom in the O–X bond play an important role in the geometry of halomethyl hydro-

halomethyl halo-peroxides and affect the C–O and O–O bond distances and the overall energetics and the thermodynamic parameters. The lowest calculated ΔH_f^0 at 298 correspond to the fluorinated methyl hydro-peroxides while the shifting of F from the methyl to the peroxide position ROOF leads to decreasing stability of the resulting isomers. The substitution of methyl hydrogens by Cl and Br produces moderately decreasing ΔH_f^0 (298) values with respect to CH_3OOH while the presence of Cl and Br in the peroxy part to give ROOCl and ROOBr type isomers, leads to a milder destabilization with respect to chloromethyl and bromomethyl hydro-peroxides compared to fluoroperoxide cases.

It is furthermore shown that these intramolecular interactions are by no means directly proportional to the structural changes and the relative strength of the various bonds but they affect the molecular properties in a more complicated way, meaning that elongation or tightening of a bond is not simply related to its strengthening or weakening. In this sense, the present findings are entirely consistent with the conclusions drawn from the study of successive chlorination of methyl hydroperoxide by Bozzelli et al. [18]. These authors have found that the elongation of the O–H equilibrium bond distance that takes place when a second and a third chlorine atom are gradually introduced into the methyl group, correlates inversely proportional to the stabilization of the species. An increase of about 6 kcal mol $^{-1}$ in the O–H bond dissociation energy was recorded each time another Cl atom is introduced [18].

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