

Ab initio and DFT investigation of fluorinated methyl hydroperoxides: Structures, rotational barriers, and thermochemical properties

S. El-Taher*

Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

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Abstract

Ab initio and density functional theory (DFT) calculations have been performed on CH_2FOOH , CHF_2OOH , CF_3OOH , CF_2ClOOH , and CFCl_2OOH . Geometries of stable conformers are optimized at the MP2(FULL)/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory. The enthalpies of formation ($\Delta H_{f,298}^\circ$) and the ROO–H, RO–OH, and R–OOH bond dissociation enthalpies (BDEs) are estimated for each of the studied hydroperoxides using the calculated reaction enthalpies ($\Delta H_{\text{rxn},298}^\circ$) of the adopted isodesmic reactions. The results show that the progressive fluorine substitution of hydrogen atoms in methyl group results in an increase in each of BDE(O–H), BDE(O–O), and BDE(C–O). This has been explained in terms of the stabilizing influence of fluorine-substituted methyl groups. However, the replacement of F by Cl when going from CF_3OOH to CFCl_2OOH leads to a decrease in both BDE(O–O) and BDE(C–O). Potential energy barriers for internal rotation about C–O and O–O are calculated at the B3LYP/6-31G(d,p) level for each of the studied hydroperoxides.

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1. Introduction

Alkyl hydroperoxides are important intermediates in the initial stages of combustions [1] and in the atmospheric photochemical oxidation of hydrocarbons [2,3]. They are produced in the reactions of alkylperoxy radicals, ROO^\bullet , with the hydroperoxy radical, HOO^\bullet [4–6]. Knowledge of the structures and thermochemical parameters for these species is thus essential for studying autooxidation in chemistry of combustion and flames, in atmospheric chemistry, and in biochemical oxidations, and for understanding and predicting their reaction pathways and rate constants in these processes. Unfortunately, there are no experimental studies of the structures and thermochemical properties of halogenated alkyl hydroperoxides; the instability and the rapid interconversion of conformers of alkyl hydroperoxides lead to complexities in studies of these species. To our knowledge, there exists only experimental determination of some thermochemical parameters for HOOH and CH_3OOH [7,8]. Theoretical investigations of

structures, vibrational frequencies, and thermodynamic properties of methyl [9,10], α -chlorinated ethyl [11], and chlorinated methyl [12–14] hydroperoxides have been performed. Concerning the fluorinated methyl hydroperoxides, there is a theoretical estimate of the heat of formation and internal bond energies of only CF_3OOH [15].

In this work, we carry out ab initio and DFT calculations for the structure, internal rotation barriers, and thermodynamic properties for the fluorinated methyl hydroperoxides CH_2FOOH , CHF_2OOH , CF_3OOH , CF_2ClOOH , and CFCl_2OOH . The effects of halogen substituent (F, Cl) on the structure and computed thermochemical parameters are investigated. The thermochemical data are evaluated against available experimental values and earlier computational results. The performance of the density functional theory (DFT) methods in determining structures and energetics for the studied compounds is justified.

2. Results and discussion

2.1. Geometries

Table 1 shows selected geometrical parameters of the studied hydroperoxides calculated at MP2(FULL) and B3LYP,

* Present address: Teachers College in Dammam, P.O. Box 2375, Dammam 31451, Saudi Arabia.

E-mail address: sabry_ea@yahoo.com.

Table 1

Calculated structural parameters of studied fluoromethyl hydroperoxides at MP2 and B3LYP levels of theory using 6-31G(d,p) basis sets

Parameters ^a	CH ₃ OOH		CH ₂ FOOH		CHF ₂ OOH		CF ₃ OOH		CF ₂ ClOOH		CFCl ₂ OOH	
	X4 = X5 = X6 = H		X4 = F, X5 = X6 = H		X4 = H, X5 = X6 = F		X4 = X5 = X6 = F		X4 = Cl, X5 = X6 = F		X4 = F, X5 = X6 = Cl	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
R(C1–O2)	1.4188	1.4168	1.3857	1.3832	1.3541	1.3752	1.3776	1.3778	1.3794	1.3766	1.3892	1.3765
R(C1–X4)	1.0872	1.0946	1.3841	1.3835	1.0777	1.0953	1.3322	1.3322	1.7494	1.7838	1.3461	1.3363
R(C1–X5)	1.0883	1.0978	1.0866	1.0943	1.3224	1.3606	1.3325	1.3330	1.3385	1.3454	1.7574	1.7834
R(C1–X6)	1.0895	1.0960	1.0876	1.0957	1.3321	1.3475	1.3425	1.3437	1.3493	1.3345	1.7738	1.8130
R(O2–O3)	1.4685	1.4565	1.4635	1.4546	1.3899	1.4520	1.4571	1.4480	1.4629	1.4563	1.4532	1.4512
R(O3–H7)	0.9690	0.9713	0.971	0.973	0.9478	0.9736	0.9711	0.9737	0.9716	0.9739	0.9722	0.9746
∠(O2–O3–H7)	98.42	99.85	99.20	100.30	102.67	100.35	99.23	100.25	99.11	100.08	99.24	100.03
∠C1–O2–O3	104.53	106.09	105.79	107.27	109.46	108.20	105.51	107.07	105.48	106.73	107.39	107.96
∠(O2–C1–X4)	104.33	104.61	110.75	111.06	106.61	105.24	105.07	105.30	105.35	104.95	102.64	112.03
∠(O2–C1–X5)	111.02	111.88	111.29	111.43	111.84	110.88	112.80	112.85	112.15	111.44	112.92	104.11
∠(O2–C1–X6)	111.41	111.45	104.57	104.53	110.60	112.63	111.81	111.69	111.05	112.62	111.84	112.24
∠(X4–C1–O2–O3)	177.43	177.05	–71.67	–73.05	179.64	–179.91	179.66	–179.92	179.87	–179.91	178.75	56.66
∠(X5–C1–O2–O3)	58.98	58.74	48.31	47.37	58.83	–60.67	60.17	–60.33	59.28	–60.86	61.12	175.41
∠(X6–C1–O2–O3)	–63.71	–64.29	170.81	169.21	–60.59	59.47	–61.80	61.57	–60.62	60.13	–64.85	–64.38
∠(C1–O2–O3–H7)	121.37	115.12	89.26	88.66	97.75	89.60	101.34	–98.75	98.83	97.59	102.90	102.28

^a Distances in angstroms and angles in degrees.

using the 6-31G(d,p) basis set. The MP2(FULL)/6-31G(d,p) structures are depicted in Fig. 1 together with the numbering system. The MP2 (B3LYP) geometry parameters of methyl hydroperoxide (CH₃OOH) are calculated to be $r_{\text{CO}} = 1.419 \text{ \AA}$ (1.417 \AA), $r_{\text{OO}} = 1.469 \text{ \AA}$ (1.457 \AA), $r_{\text{OH}} = 0.969 \text{ \AA}$ (0.971 \AA), $\angle \text{OOC} = 104.5^\circ$ (106.1°), $\angle \text{OOH} = 98.4^\circ$ (99.9°), and $\angle \text{COOH} = 121.4^\circ$ (115.1°), which are in good agreement with experimentally determined data of $r_{\text{CO}} = 1.437 \text{ \AA}$, $r_{\text{OO}} = 1.443 \text{ \AA}$, $r_{\text{OH}} = 0.969 \text{ \AA}$, $\angle \text{OOC} = 105.7^\circ$, $\angle \text{OOH} = 99.6^\circ$, and $\angle \text{COOH} = 114^\circ$ [25]. The results show that the B3LYP method is more accurate than the MP2 in predicting $\angle \text{OOC}$, $\angle \text{OOH}$, and $\angle \text{COOH}$ angles.

In general, both MP2 and B3LYP predict decreases in the C–O and the O–O bond lengths as a result of fluorine substitution. The C–O bond length decreases 0.033 \AA (MP2) and 0.034 \AA (B3LYP) for the first fluoro substitution, then further decreases of 0.032 \AA (MP2) and 0.008 \AA (B3LYP) for the difluoro substitution. However, when going from CHF₂OOH to CF₃OOH, the C–O bond length increases 0.024 \AA (MP2) and 0.008 \AA (B3LYP). For the O–O bond, the MP2 (B3LYP) method predicts shortenings of 0.005 \AA (0.002 \AA) and 0.074 \AA (0.003 \AA) on going from CH₃OOH to CHF₂OOH. While the B3LYP predict further decrease of 0.004 \AA for the trifluoro, a significant increase of 0.067 \AA is predicted by the MP2 method. The shortening in the C–O and O–O bonds when going from CH₃OOH to CHF₂OOH may be explained in terms of an anomeric-type effect [17], where the electronegative fluorine atoms inductively stabilize the π -acceptor orbitals of CH₂F and CHF₂ groups leading to a stabilizing geminal interaction with the π -donor orbitals (lone pairs) of OOH (or OH) moiety. This interaction leads, in turn, to a shortening of 0.004 \AA in the C–F bond, compared to that of CH₃F. In CHF₂OOH, the geminal interaction between the two fluorine atoms themselves results in further lowering in the energy of the π -acceptor orbital of the CHF₂ group, and hence large stabilizing interaction between

the CHF₂ group and the OOH (or OH) moiety. As a result of that, C–O, O–O, and C–F bonds are substantially shortened by 0.065, 0.079, and 0.062 \AA as compared to those of CH₃OOH and CH₃F, respectively. On the other hand, the lengthening in the C–O and O–O bonds when going from CHF₂OOH to CF₃OOH may be due to unfavorable interactions between the three fluorine atoms which decrease the extent of interaction between the CF₃ and OOH (or OH) groups, compared to that of CHF₂OOH. It is worth noting that the substitution of F by Cl lengthens (destabilizes) the C–O and O–O bonds. Such destabilization may be explained in terms of the unfavorable Cl–F geminal interactions, in addition to the steric hindrance that might be introduced by the bulky chlorine atoms.

2.2. Enthalpies of formation

The enthalpy of formation of CH₃OOH has been previously reported [9–14,26]. For the sake of verifying the accuracy of the adopted methods of calculation, the general isodesmic reaction:



is selected to further estimate $\Delta H_{\text{f},298}^\circ$ for CH₃OOH using the experimentally determined enthalpies of formation of HOOH, CH₃CH₃, and CH₄ to be -32.48 ± 0.05 [27], -20.04 ± 0.07 [27], and -17.9 ± 0.1 kcal/mol [28], respectively. The enthalpy of formation for CH₃OOH has been reported to be -31.71 kcal/mol [10] determined via atomization energy at G2 level of theory, -31.64 kcal/mol calculated at a CBSQ//B3** level [14], and -31.4 ± 1.0 kcal/mol [26] using group additivity method. Our calculated $\Delta H_{\text{f},298}^\circ$ of CH₃OOH are found to be -34.39 and 32.31 kcal/mol, at B3LYP/6-31G(d,p) and B3LYP/6-311+G(2df,2p) levels, respectively. These values are in good agreement with the experimental value, -33.2 ± 1.9 kcal/mol [13]. The $\Delta H_{\text{f},298}^\circ$ for CH₃OOH is overestimated by 3.12 kcal/mol

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