Quantum Mechanical Studies of Isomeric and Conformeric Structures of Methyl-Chloro-Peroxide

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ABSTRACT: Ab initio quantum mechanical studies are carried out for the isomeric structures and the torsional potential of methyl-chloro-peroxide. These species are important intermediates in the atmospheric reactions of methyl, methoxy, and methylperoxy radicals with chlorine dioxide, chlorine monoxide, and atomic chlorine, respectively. The calculations indicate that the peroxide form, CH_3OOCl, with a skew geometry for C, O, O, and Cl atoms, is the lowest minimum energy structure followed by CH_3OClO. The CH_3ClO_2 adduct is found to be much higher in energy. The calculated isomerization barriers are found to be relatively high to permit possible interconversion pathways. © 2004 Wiley Periodicals, Inc. Int J Quantum Chem 98: 335–341, 2004

Key words: ab initio; methyl-chloro-peroxide; torsional barrier; isomerization barrier; electronegativity

Introduction

Methyl-chloro-peroxide, CH_3OOCl, is an interesting species, the methyl analogue of the well-studied hydro-chloro-peroxide, HOOCl. Along with the isomeric CH_3OClO adduct, they are the two important intermediates formed in the reactions CH_3+OClO, CH_3O+ClO and CH_3O_2+Cl, which have been suggested to play a significant role in the atmospheric chemistry of Cl atoms and CH_3 and ClO radicals [1, 2] and have been the subject of several experimental studies [3–7]. However, contrary to the extensive investigations of HOOCl isomers [8–10], much less attention has been given to its methyl analogue [11].

In the present work, we carry out quantum mechanical calculations of the isomers of CH_3OOCl and the associated isomerization and conformational barriers. The calculated structural and energetics characteristics allow a detailed comparison of the similarities and differences of CH_3OOCl with a number of other XOOCl peroxides, X=H, Cl, Br, I [8–10, 12–26] and provide another opportunity to

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discuss the structural and relative stability trends in various Cl—O bond containing species.

Quantum Mechanical Calculations

A total of three minimum energy structures, two isomerization transition states, and two torsional barriers were investigated. All minimum energy and transition state geometries have been fully optimized at the UMP2(full)/6-311G(d, p) level of theory. Harmonic frequencies have also been calculated at the same level to characterize the various structures; IRC calculations were performed to confirm that each isomerization transition state is linked to the desired species. Isomerization transition states and cis- and trans-torsional barriers were characterized by one imaginary frequency as first-order saddle points. G2MP2 [27] calculations were further carried out at the UMP2(full)/6-311G(d, p) optimized geometries to improve the energetics of the system. The G2MP2 method, which is a modified version of G2 [28], using MP2 instead of MP4 for the basis set extension corrections, is believed to make a reasonable approximation of the full G2 method, taking into account the substantially reduced computational cost. All calculations were performed using the Gaussian 98 series of programs [29].

Structural and Frequency Results

Tables I–III summarize the calculated optimized structures and the harmonic frequency results. The calculated structures are also depicted in Figure 1, while the structural changes accompanying the conformational potential are depicted in Figure 2.

The ground state of CH_3OOCl is found to exhibit a skewed geometry with respect to C, O, O and Cl atoms, analogous to the hydro-chloro-peroxide species, HOOCl. It presents a COOCl dihedral angle of 88.0° and a O—O bond distance of 1.405 Å at the present MP2/ 6-311G(d, p) level of theory, which compare well with the corresponding features of the HOOCl adduct, the dihedral angle of 88.7°, and the O—O equilibrium distance of 1.410 Å at the B3LYP/ 6-311++G(3df, 2pd) level of theory [10]. Comparison with structural features of other chloro-peroxides is also profitable. For instance, the O—O equilibrium distance of 1.405 Å in CH_3OOCl at the present MP2/ 6-311G(d, p) level of theory is also consistent with the corresponding O—O bond

TABLE I

Optimized geometries (Å, deg) for CH_3OOCl isomers at the UMP2(full)/6-311G(d, p) level of theory.

	CH_3OOCl	CH_3OClO'	CH_3ClO_2
r(OO)	1.405		
r(CO)	1.421	1.430	
r(OCl)	1.761	1.760	
r(ClO')		1.520	1.488
r(CCl)			1.794
r(CH)	1.092	1.090	1.088
r(CH')	1.094	1.096	1.089
r(CH")	1.091	1.096	1.088
<HCO	110.7	111.7	
<H' CO	104.2	105.3	
<HCCl			107.8
<H' CCl			102.1
<COO	107.5		
<OOCl	109.5		
<COCl		108.6	
<OClO'		113.8	
<CClO			101.4
Ê (COOCl)	88.0		
Ê (HCOO)	175.5		
Ê (H' COO)	56.6		
Ê (COClO')		71.4	
Ê (HCOCl)		176.3	
Ê (H' COCl)		57.1	
Ê (H' CClO)			178.4

length, 1.412 Å and 1.416 Å in BrOOCl and ClOOCl, respectively, at the MP2/AREP-TZ(2df) level [20]. The Cl—O bond distance of 1.761 Å also compares favorably with the corresponding 1.757 Å bond distance in BrOOCl at the B3LYP/6-311++G(3df, 3pd) level [18] and the OOCl bond angle in CH_3OOCl, 109.5°, assumes a similar value with the corresponding values, 109.0° and 108.9° in BrOOCl and ClOOCl, respectively, at the MP2/AREP-TZ(2df) level [20].

The other two important energy minima are the hypervalent CH_3OClO' and CH_3ClO_2 structures. The CH_3OClO' structure presents a COClO dihedral angle of 71.4°, in fair consistency with the dihedral angle 75.7° in HOClO' at the B3LYP/6-311+G(3df, 2p) level of theory [10] and the dihedral angle 72.0° in ClOClO at the MP2/AREP-TZ(2df) level [20]. Generally, a wider spread in dihedral angle values is observed in the literature than for the other structural features in various XOOY isomers. In a detailed comparison of MP2 and B3LYP structural results for chlorine, bromine, and mixed chlorine/bromine oxides, Gomez and

TABLE II
Optimized geometries (Å, deg) for CH$_3$OOCl conformational and isomerization barriers.

	CH$_3$OOCl(*cis*)	CH$_3$OOCl(*trans*)	TS1	TS2
r(OO)	1.498	1.491	1.520	—
r(CO)	1.414	1.420	1.440	2.051
r(OCl)	1.716	1.704	2.081	1.495
r(ClO′)			1.917	1.602
r(CH′)	1.088	1.089	1.091	1.093
r(CH)	1.088	1.087	1.121	1.084
<HCO	112.6	111.1	110.7	134.2
<H′ CO	101.4	103.7	104.2	82.5
<HCCl				94.6
<H′ CCl				121.7
<COO	115.2	101.5	104.2	
<OOCl	115.0	104.1	74.5	
<COCl				68.6
<OClO′				114.2
<CClO				134.0
Ê (COOCl)	0.0	180.0		
Ê (H′ COO)	180.0	180.0		
Ê (HCOO)	63.1	61.1		
Ê (COClO′)			139.7	−129.3
Ê (H′ COCl)			−100.9	154.4

Pacios [20] noted a clear tendency for B3LYP calculations to overestimate the dihedral angle. CH$_3$OClO′ presents other interesting characteristics analogous to other XOClO′ adducts. Most significantly, it shows the considerable shrinkage in the equilibrium distance of the terminal ClO′ bond compared with OCl distance, due to the partial double bond character between the hypervalent Cl atom and the terminal oxygen. As a result, the OCl and ClO′ bond lengths are found to be quite differ-

TABLE III
Harmonic vibrational frequencies in cm^{-1} of isomeric and conformeric forms of CH$_3$OOCl.*

CH$_3$OOCl	3309(9), 3178(25): CH$_3$ asym. stretch, 3083(19): sym. stretch, 1530(13), 1487(9): CH$_3$ asym. deformation, 1477(0): sym. deformation, 1237(3), 1200 (2): CH$_3$ rock, 1048(36): CO stretch, 838(32): OO stretch, 620 (27): OCl stretch, 486(2): COO bend, 350 (6): OOCl bend, 218(2): CH$_3$ twist, 135 (2): torsion
CH$_3$OClO′	3194(7), 3135(29), 3045(34), 1529(18), 1491 (9), 1480(2), 1202(2), 1188(4), 1119 (114): ClO′ stretch, 1043(58): CO stretch, 466 (118): OCl stretch, 411(28): COCl bend, 253(17): OClO′ bend, 178(3): CH$_3$ twist, 88(18): torsion
CH$_3$ClO$_2$	3254(0), 3245(1), 3110(2), 1460(11), 1445(9), 1375(8), 1136(251), 1052(47), 1018(3): ClO asym. stretch, 1008(80): ClO sym. stretch, 687(31): CCl stretch, 473(24): OClO′ bend, 400(17): CClO asym. bend, 340(1): CClO sym. bend, 230(0): HCClO torsion
CH$_3$OOCl (*cis*)	3238, 3227, 3120, 1576, 1523, 1489, 1226, 1189, 1060, 759, 704, 473, 304, 295, 233i
CH$_3$OOCl (*trans*)	3251, 3223, 3122, 1578, 1522, 1494, 1233, 1205, 1067, 832, 780, 407, 270, 237, 41i
TS1	3255, 3231, 3114, 1532, 1507, 1470, 1202, 1179, 1087, 889, 531, 407, 267, 221, 1530i
TS2	3335, 3269, 3120, 1557, 1483, 1320, 1192, 1059, 948, 871, 487, 358, 217, 170, 935i

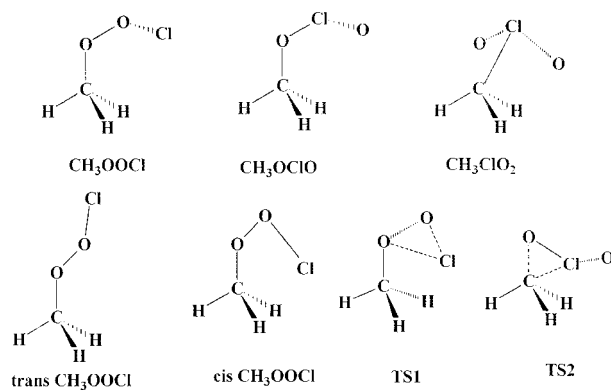* Numbers in parentheses give the IR intensities.

FIGURE 1. Optimized structures of CH_3OOCl isomers, cis- and trans-conformers and isomerization transition states, TS1 = [$CH_3OOCl \leftrightarrow CH_3OClO$] and TS2 = [$CH_3OClO \leftrightarrow CH_3ClO_2$].

ent, 1.762 Å and 1.519 Å, respectively, in analogy with the corresponding values 1.792 Å, 1.489 Å and 1.807 Å, 1.489 Å in $BrOClO'$ and $ClOClO'$, respectively, at the MP2/AREP-TZ(2df) level [20]. Another interesting feature to mention is the larger value of the $OClO'$ bond angle compared with the $COCl$ bond angle, resulting from the larger repulsion between the two oxygen atoms compared with the repulsion between C and Cl atoms, a situation exactly analogous with $OClO'$ and $HOCl$ bond angles in $HOClO'$ adduct [8–10].

The effect of the multiple bond character in the $Cl—O$ bond is enhanced in the third isomer, CH_3ClO_2, which lies much higher in energy with respect to CH_3OOCl and presents the shortest ClO bond distance, 1.488 Å. This is in excellent agreement with the corresponding ClO bond distances observed in $HClO_2$, 1.488 Å and 1.480 Å, using MP2 methodology [8], but significantly larger than the ClO values observed in $BrClO_2$ and $ClClO_2$ [20], using both MP2 and B3LYP methodologies, 1.441 Å, 1.460 Å, and 1.441 Å, 1.453 Å, respectively [20]. The difference probably reflects the considerably higher stability of $BrClO_2$ and $ClClO_2$ species as opposed to $HClO_2$, CH_3ClO_2, as we shall see below. The $CClO$ bond angle, 101.4°, is also in consistency with the $HClO$ bond angle, 101.5°, in the corresponding $HClO_2$ isomer [8–10]. Finally, in all isomers the methylic hydrogens are placed in an analogous manner. In the peroxide form one hydrogen atom is about coplanar with C, O, and O atoms and the other two are placed symmetrically around this plane. Similarly, in CH_3OClO' one hydrogen atom is near coplanar with C, O, and Cl atoms. In the

CH_3ClO_2 isomer, one H is found coplanar with C, Cl and one of the two terminal oxygens.

Harmonic frequencies for the three isomers are listed in Table III. They are in general consistency with the corresponding modes of MP2 results for HOOCl [8–10] and XOOY (X,Y = Cl, Br) isomers [20]. For instance, the present values for O—O, O—Cl, and Cl—O' stretchings, 838, 620, and 1119 cm^{-1}, agree within 15% with the corresponding values of the quoted species. Discrepancies are very often observed for the torsional mode, since torsional frequencies are usually lower compared with the other frequencies, and they are always difficult to reproduce accurately.

The two conformeric cis- and trans-structures with respect to C, O, O, and Cl atoms are well characterized as torsional barriers by the imaginary frequencies, 233i and 41i, respectively, listed in Table III. The cis-configuration exhibits a much larger absolute value of the imaginary frequency compared with the trans-configuration, indicating a much tighter energy barrier for the cis-geometry. Interesting structural changes in both ClO and OO bond lengths accompany the torsional potential, as shown in Figure 2. These bond distances decrease
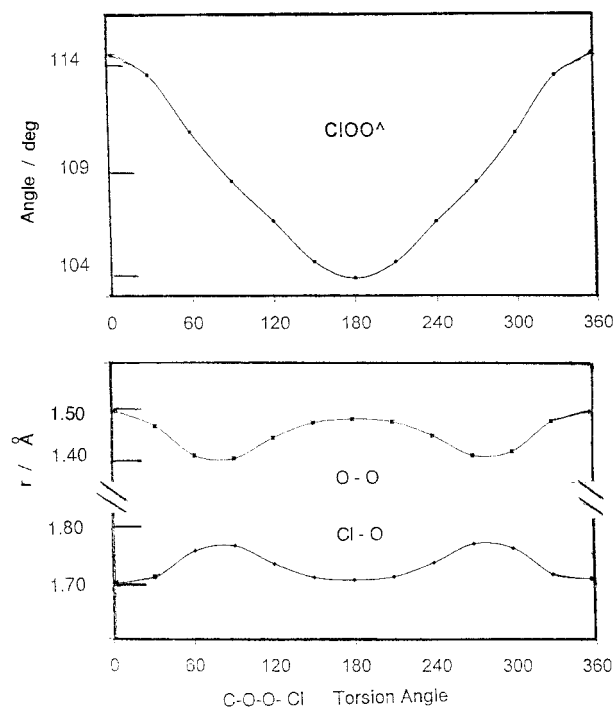

FIGURE 2. Variation of bond angle ClOO (top) and Cl—O, O—O bond distances (bottom) vs C—O—O—Cl torsional angle.

TABLE IV _____

Total electronic (Hartrees) and relative energies (kcal mol^{-1}) for isomers and conformers of CH_3OOCl.

Species	MP2/6-311G(d, p)	ΔE	G2MP2	ΔE
CH_3OOCl	−649.397128	0.0	−649.656724	0.0
CH_3OClO	−649.354694	26.6	−649.643332	8.4
CH_3ClO_2	−649.292753	65.5	−649.607629	30.8
TS1	−649.348747	30.3	−649.613932	26.8
TS2	−649.287313	68.9	−649.605672	32.0
CH_3OOCl (cis)	−649.380056	10.7	−649.641974	9.2
CH_3OOCl (trans)	−649.391459	3.6	−649.651848	3.1

and increase, respectively, in going from the minimum energy skew configuration to the cis- and trans-geometries. More specifically, the peroxide bond O—O assumes the shortest value in the equilibrium configuration where the Cl—O length takes on its maximum value. The changes reflect the weakening of the O—O bond in both conformational positions, as well as the effect of the methyl group-chlorine atom repulsions. When comparing the magnitude of the variations in O—O and Cl—O bond distances in Table II and Figure 2, however, we readily see that they are more pronounced in the O—O bonding, 1.405 Å to 1.498 Å, than in the Cl—O bonding, 1.704 Å to 1.761 Å. This suggests, as pointed out by Gomez and Pacios [16], that the OO bonding is the dominant factor in the torsional barriers of XOOY peroxides, while the role played by ClO bonding is much less important. Finally, comparing the ClO distance in cis- and trans-geometries, we can see from Table II and Figure 2 that it is larger in the cis- than in the trans-configuration, as in HOOCl [8], and the opposite of the ClOOCl case [16].

The variation of the ClOO bond angle also included in Figure 2, shows again significant changes and varies from a maximum value in the cis-configuration, 115.2° to a minimum value in the trans-configuration, 101.5° with an intermediate value, 107.5° in the equilibrium geometry. The COO angle also varies in a similar way, as we can see from Tables I and II. Finally, the rotation of the methylic hydrogens about the C—O bond in any configuration presents alternative energy maxima and minima every 60° as in methyl-hydro-peroxide [29].

ENERGETIC AND RELATIVE STABILITY RESULTS

The total electronic and relative energies are summarized in Table IV. The relative stability between the three isomers is a very interesting issue and relates to the nature of ClO bonding in $XClO_2$ species in general [30]. In the present case, the most stable isomer is the peroxide form followed by CH_3OClO, which lies only 8.4 kcal mol^{-1} higher than CH_3OOCl at the present G2MP2 level of theory. Such a difference is consistent for instance with HOClO lying 7 kcal mol^{-1} higher than HOOCl at the G2M(CC2)//B3LYP/6-311++G(3df, 2pd) level [10]. The CH_3ClO_2 form is calculated to be the most unstable, higher than CH_3OOCl by about 31 kcal mol^{-1}, lower however, compared with the energy difference between HOOCl and HClO$_2$, around 50 kcal mol^{-1} [8–10]. In other chloro-peroxide families, as in ClOOCl, for instance, the $ClClO_2$ isomer is the next stable isomer after ClOOCl, lying very near the peroxide form [12, 13]. Data on the stability of several ($XClO_2$) isomers are summarized for comparison in Table V. Although the results derived with different methodologies and varying sizes of basis sets, they can still give a rough estimation and an approximate idea about the relative stabilities of the quoted species among various families. For X=H, CH_3 and I, the $XClO_2$ forms are found to be the most unstable structures with increasing stability as we go from H to I. In contrast, for X=Cl and Br, i.e., $ClClO_2$ and $BrClO_2$, are very stable, the next stable structures after the corresponding peroxide isomer ClOOCl and BrOOCl.

The stability trends of $XClO_2$ isomeric forms are directly related to the nature of chlorine oxygen bonding in hypervalent chlorine compounds. In the analysis of chlorine and bromine oxygen bonding, Lee et al. [31] have found that these bonds are highly ionic in nature and that chlorine or bromine are very positively charged. The largest ionic character was found for the ClO and BrO bonds in $XClO_2$ and $XBrO_2$, larger than for ClO′ and BrO′ in

TABLE V

Relative stabilities of isomers and conformers of XOOCl peroxides (X=H, CH₃, Cl, Br, I) (kcal mol⁻¹).

Species[a]	ΔE_1	ΔE_2	ΔE_3	ΔE_4
HOOCl[b]	51.0	8.3	5.1	3.4
CH₃OOCl	30.8	8.4	9.2	3.1
IOOCl[c]	22.6	12.4	8.4	2.9
ClOOCl	3.4[d]	13.3[d]	9.1[e]	5.1[e]
			10.1[f]	5.4[f]
BrOOCl	6.8[g]	10.5[g]	8.7[h]	4.3[h]
			10.4[i]	5.0[i]

[a] ΔE_1, ΔE_2 represent the relative stabilities of XClO₂ and XOClO with respect to XOOCl, respectively, and ΔE_3, ΔE_4 are the cis- and trans-conformational barriers.
[b] Ref. [8].
[c] Refs. [22, 23, 25].
[d] Ref. [12].
[e] Ref. [15].
[f] Ref. [16].
[g] Ref. [18].
[h] Ref. [26].
[i] Ref. [21].

XOClO′ and XOBrO′, because the halogen atom possesses five bonds and effectively loses electron density through the sharing of its lone-pair p electrons in the latter cases. This fact has an immediate impact on the thermodynamic stability of the various species under consideration. The positively charged Cl atom makes the XClO₂ isomers increasingly stabilized as the electronegative character of X fragment increases, something that explains the striking degree of stabilization in going from X=H to X=Br. The same phenomenon has been observed in the XOOBr series [32]. For instance, the HBrO₂ isomer lies 53.8 kcal mol⁻¹ above HOOBr, while BrBrO₂ lies only 6.8 kcal mol⁻¹ above BrOOBr [18].

Table V also includes the energy barriers for hindered rotation for a number of XOOCl peroxides. The barriers in all cases are comparable to the cis-barrier, always found to be higher than the trans-barrier.

Isomerization Processes

Two transition state structures were determined for isomerization among the three isomers. The first one is found for CH₃OOCl ↔ CH₃OClO isomerization, labeled TS1, with an imaginary frequency, 1530i and lying 26.8 kcal mol⁻¹ above CH₃OOCl.

Again, the comparison with the corresponding transition state structure for HOOCl↔HOClO isomerization is useful and indicates similar geometries, although the associated barrier height in the HOOCl↔HOClO case is located much higher, 39.3 kcal mol⁻¹ above HOOCl [10]. The structure as depicted in Figure 1 assumes a three-member ring geometry and results from the loosening of the OO bond, which becomes 1.520 Å, and the gradual formation the OCl bond becoming 2.081 Å.

A second transition state configuration, TS2, has been determined for the CH₃OClO ↔ CH₃ClO₂ isomerization process. The structure results from the loosening of the C—O bond, 2.051 Å and parallels the corresponding structure for the HOClO ↔ HClO₂ process. However, it also lies much lower, 23.6 kcal mol⁻¹ above CH₃OClO compared with 67.6 kcal mol⁻¹ [10] in the hydroxy case. This is a notable difference with the hydroperoxide series, and it is the consequence of the breaking of the C—O bond compared with the breaking of the stronger H-O bond.

The calculated high barriers for conversion of one isomer to the other do not allow interisomerization processes to play a role in the mechanism of CH₃O+ClO and CH₃+OClO reactions [5, 11].

Summary

The present work contains the calculated structures, harmonic frequencies, and energetics of isomeric structures of methyl-chloro-peroxide and the isomerization and conformational barriers. The calculations indicate that the structural and frequency results are in consistency with the analogous results for a number of other chloro-peroxides and similar trends in the geometrical and frequency characteristics are followed as in the case of hydro-chloro-peroxide and the chloro- and mixed Cl/Br analogues.

Regarding the energy stability ordering among the various isomers, the skew configuration of the peroxide isomer is found to be the lowest energy structure followed by CH₃OClO. The third isomer, CH₃ClO₃ lies much higher in energy. The calculated energetics of methyl-chloro-peroxide isomers resemble closely the corresponding results of (CH₃BrO₃) system and provide further supporting evidence about the stability ordering trends of the various isomeric forms of XOOCl peroxides, fully complying with the highly ionic character of ClO bonding in XClO₂ species.

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