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Theoretical study of valence isomerization in the $HOCl_2$ system

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Abstract

Hartree–Fock level and post Hartree–Fock level molecular orbital calculations are reported for the HOOCl and HOClO molecules. The calculations indicate that the HOOCl isomer is more stable than the HOClO form. Geometries have been determined at the HF/6-311G(d,p) level, together with vibrational frequencies, rotational constants and electrical moments. A discussion of the chemical bonding within the molecules is presented.

Introduction

The HOOCl molecule, hydroperoxy chloride, and the HOClO molecule, chlorous acid, are possible products of coupling reactions which may occur via reactant–reactant coupling between the ClO_x and the HO_x cycles in stratospheric ozone depletion [1, 2]. The first would be the reaction product of the reaction of the hydroperoxy radical with free chlorine atoms and the second would arise via the reaction of the hydroxy radical with the ClO radical. For the past two years we have been involved in the study of such coupling reactions and in the course of these studies we have investigated these valence isomers of the $HClO_2$ system. In this paper we shall focus upon the structure of these two molecules, their relative energetics, and their spectroscopic and other physical properties.

Calculations

The calculations reported herein are of two distinct types, Hartree–Fock Self Consistent Field calculations [3, 4] and Moeller–Plesset Perturbative type carried out through fourth order [5, 6]. All calculations were carried out on a CRAY 2 computer at the National Center for Supercomputing Activities using the Gaussian 88 computer software [7]. The geometries of the isomers were optimized using the 6-311G(d,p) basis set at the Hartree–Fock level [8] and utilized the Berny algorithm [9]. Post Hartree–Fock calculations were carried out through fourth order using this same basis set and included the contributions from all 'singles, doubles, triples and quadruple' excitations from the reference function [10, 11]. The HF/6-311G(d,p) geometry was utilized throughout. Vibrational analysis was carried out using analytically calculated derivatives and the FG matrix method [12, 13]. The largest basis set employed, the 6-311G(df,p) set, was used for a second order calculation [14], and the result obtained used to estimate the effects of performing a full fourth order calculation via the additivity suggestion of McKee and Lipscomb [14]. The use of the large basis sets is required to allow for the hypervalent tendencies of the chlorine atom in order to obtain a proper geometry for the molecules [15]. One cannot be certain that we have allowed the calculation to lead to realistic geometry unless they are included in the calculation.

Results and discussion

Geometries and electronic structure

The geometries calculated for the two valence isomers are shown in Table 1. The calculated bond orders and gross atomic charges from a Mulliken type population analysis are presented in Table 2 [16].

The HOOCl molecule has a somewhat unexpected geometry. The chlorine–oxygen distance is calculated to be 1.68 Å. The same distance in the chlorine dioxide molecule is found to be 1.49 Å [15], while

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TABLE 1. Calculated geometries[a] for HOOCl and HOClO

Molecule	Distances (Å)			Angles (°)		
	ClO	OO	HO	ClOO	HOO	Dihedral[b]
HOOCl	1.680	1.364	0.946	110.1	103.6	92.0
	ClO(H)	ClO	HO	OClO	HOCl	Dihedral
HOClO	1.641	1.535	0.948	109.6	106.4	62.8

[a] Geometries are based upon the results of Hartree–Fock calculation using the 6-311G(d,p) basis set. [b] This is the angle formed by the HO bond and the plane defined by the chlorine atom and the two oxygen atoms.

TABLE 2. Population analysis and dipole moments

	Atom charges	Bond orders	Dipole moment
HOOCl			
H	0.289	H–O 0.043	2.00 Debye
O(H)	−0.258	O–O 0.002	
Cl	0.177	Cl–O 0.045	
O	−0.209		
HOClO			
H	0.309	H–O 0.304	3.27 Debye
O(H)	−0.466	Cl–O(H) 0.020	
Cl	0.773	Cl–O 0.044	
O	−0.616		

The notation O(H) designates the oxygen atom to which the hydrogen atom is bonded.

in the chlorite ion, ClO_2^- it lengthens out to 1.64 Å as observed in the ammonium chlorite crystal [17]. Clearly our calculated distance is much closer to the latter than the former indicating that the molecule probably contains a Cl–O single bond. The oxygen–oxygen distance is calculated to be 1.36 Å, a value considerably smaller than that associated with the normal oxygen–oxygen single bond. The same distance in hydrogen peroxide [18] is observed to be 1.47 Å, while it is 1.21 Å in diatomic oxygen and 1.12 in the diatomic oxygen positive ion [19, 20].

It would seem that the hydroperoxy chloride molecule contains an oxygen–oxygen bond possessing considerably multiple bond character. The population analysis indicates that there is a considerably shift of electron charge from the chlorine atom over to the two oxygen atoms making them the electronegative centers of the molecule.

The HOClO molecule represents what is considered to be a ‘pretty normal’ tetrahedral structure. The Cl–O distance is calculated to be 1.54 Å, a value somewhat smaller than that associated with a Cl–O single bond, but the error of the calculation places it within the proper range. The Cl–O distance for the bond involving the oxygen atom bonded to the hydrogen atom is also normal at 1.64 Å. The presence of the two oxygen atoms bonded to the chlorine atom causes considerable shift of electronic charge from the chlorine atom to the oxygen atoms as evidenced by the large positive charge calculated for the chlorine atom (0.773). The bond angles calculated for the structure are very close to tetrahedral angles, non-bonded pair–non-bonded pair interactions causing the HOCl angle to be somewhat smaller than 109°. Interestingly the OClO angle, which is subject to the same effect, does not seem to show the deviation from the tetrahedral angle of simple valence theory.

The population analysis for the two species indicate a more severe separation of charges in the HOClO molecule than is present in the HOOCl molecule. This will manifest itself below where we shall examine the energetics of the two isomers.

Energetics

In Table 3 are presented the results of our calculations in terms of the relative energy of the two isomers. The calculations clearly indicate that the hydroperoxy chloride form is the more stable of the two isomers. Although the energies themselves contain considerable error, as our calculations are not large enough to include all the correlation energy, there is little question about the energy of the one

TABLE 3. Calculated energies for HOOCl and HOClO

Calculation	HOOCl[a]	HOClO[a]	Difference (kJ/mol)
HF/6-311G(d,p)	−609.6671025	−609.6120188	144.6
MP4/6-311G(d,p)	−610.2474858	−610.2044589	113.0
MP2/6-311G(df,p)	−610.2885256	−610.257163	82.4
[b]	−610.3272380	−610.2593479	178.2

[a] Hartree units. [b] This energy is obtained by the following formula:

E(MP4/6-311G(d,p) − E(MP2/6-311G(d,p) + E(MP2/6-311G(df,p).

TABLE 4. Vibrational frequencies and rotational constants

HOOCl	HOClO
Vibrational frequencies (cm^{-1})	
398.6	282.5
456.0	421.8
804.8	767.4
1140	815.2
1589	1360
4101	4087
Zero-point energy (kJ/mol)	
50.776	46.257
Rotational constants (GHz)	
54.1722	32.8070
6.45062	8.94925
5.86884	7.14871

isomer as compared to the other. We calculate the difference between isomers to be about 170–200 kJ/mol. The error associated with this result is about 40–60 kJ/mol based upon the presence of twenty valence electrons and liberally estimating an error of 2–3 kJ/mol per electron [21].

Table 4 presents the spectroscopic properties calculated for the two isomers. The vibrational frequencies presented are probably about ten percent too high and should be scaled downward. This is in accord with the well known results and experience of other workers.

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