Inorganica Chimica Acta, 111 (1986) 157–161

An *Ab Initio* Study of Valence Isomerization in the HOCl–HClO System

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Received May 23, 1985

Abstract

Hartree–Fock level and post Hartree–Fock level molecular orbital calculations have been completed for HOCl and its valence isomer, HClO. Ground state geometries have been determined for each molecule. The energy change for the reaction

$$\mathrm{HOCl} \longrightarrow \mathrm{HClO}$$

is estimated to be 67 ± 5 kcal/mol endothermic and the activation energy for the process is 74 ± 5 kcal/mol. The transition state for the reaction is identified and discussed. A vibrational analysis has been carried out for both HOCl and HClO. The calculated photoelectron spectrum is discussed for each of the molecules.

Introduction

The HOCl molecule is of interest to the atmospheric chemists, meteorologists, and gas phase kineticists for many reasons [1]. This molecule or its isomer HClO has been postulated to play a fundamental role in assessments of the effect of chlorine–oxygen containing materials on the earth's ozone layer. Leck, Cook, and Birks [2] have postulated the formation of both isomers in the reaction of ClO with the hydroperoxy radical. Although HClO has not been observed in the laboratory, the reaction

$$\mathrm{ClO} + \mathrm{HO_2} \longrightarrow \mathrm{HClO} + \mathrm{O_2} \tag{1}$$

can be exothermic provided the heat of formation of HClO is 43 kcal/mol or less than that of HOCl. Thus the relative energies of HClO and HOCl are of interest. The possibility of both isomers being present in the atmosphere, of course, introduces additional complexity into the atmospheric chemistry. Stimpfle, Perry, and Howard [3], in the study of the reaction between HO_2 and ClO, have also recognized the possibility of HClO being present as a component of a complex in a possible reaction mechanism. The possibility of HClO being formed via reaction (1) has also been recognized by Burrows and Cox [4]. The ultraviolet spectra of HOCl has been extensively studied by Molina and Molina [5], while the photodissociation of HOCl has been the focus of the recent work of Jaffe and Langhoff [6]. Theoretical study of the electronic structure of HOCl (*ab initio* CI) has been carried out by Hirsch, Bruna, Peyerimhoff, and Buenker [7, 8]. Vibrational frequencies have been previously studied by Komornicki and Jaffe (theoretical) [9] and Ashby (experimental) [10]. In this paper, we report the results of a large theoretical study in which we characterize the ground electronic states of HOCl and its isomer HClO, identify and characterize the transition state involved in the isomerization reaction, and discuss the energetics of the process. A by-product of our work includes a vibrational analysis for each isomer and here we compare to previous theoretical work and experimental studies.

Calculations

The calculations reported herein are of two types, Hartree–Fock Self Consistent Field type [11] and Perturbative Calculations employing the Moller–Plesset formulas [12]. All calculations were carried out using the Gaussian 82 computer program [13] on the VAX 11/780 or Cray 1 computers. The reported geometries were optimized employing the 6-31G(d, p) basis set [14] and the Fletcher–Powell minimization algorithm*. All minima and the transition states saddle point were confirmed by examination of the eigenvalue of the force constant matrix.** Post Hartree–Fock calculations were carried through fourth order including all triple substitutions [16] using the geometry obtained from the HF/6-31G(d) calculations. The frozen core approximation was not used. The vibrational analysis was carried out using

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*A quadratic procedure is used to locate minima using a continual updating of the Hessian matrix and using computed first derivatives [15].

**A saddle point is characterized by the occurrence of one and only one negative eigenvalue for the force constant matrix.

0020-1693/86/$3.50

the Wilson FG matrix method [17]. The largest calculations reported made use of the completely polarized double zeta, 6-311G(d, p), basis set [18]. This was necessary as it is well known that the use of a polarized basis set leads to more reliable geometries for molecules containing hypervalent third row elements such as Cl, S, and P [19]. Although HOCl and HClO are not normally considered to be hypervalent molecules [20], we cannot *a priori* be certain that this is also true for the transition state characterizing the minimum pathway between the two isomeric forms.

Results and Discussion

The geometries calculated for HOCl and HClO are shown in Table I. Two sets of geometries are shown that were obtained using a minimal split level basis set, the 3-21G, and that obtained using the larger 6-31G(d) basis set. Significant differences exist between the two calculated geometries. The bond distances calculated with the latter basis set are considerably shorter than those obtained in use of the 3-21G set. For example, in HOCl the Cl–O distance drops from 1.767 Å to 1.670 Å while the H–O distance decreases to 0.9512 Å from 0.9747 Å. In HClO a very large decrease in the Cl–O distance is observed 2.2986 Å to 1.723 Å in passing from the smaller basis set to the larger set. In both isomers these results illustrate the important role by the harmonic d functions of the chlorine atoms. The best experimental geometry determination for HOCl yielded an O–H distance of 0.975 Å, a Cl–O distance of 1.689 Å, and a bond angle of 104.8 deg [21]. Previous calculated results yielded 0.947 Å for O–H and 1.667 Å for Cl–O with a bond angle of 105.6° (Kormornichi and Jaffe) [9] and 0.969 Å for O–H, 1.691 Å for Cl–O with a bond angle of 102.4° [8]. The calculated 6-31G(d) geometry is in excellent accord with the experimental, the Cl–O distance being only 0.019 Å shorter than the observed distance and the calculated bond angle differing less than one degree from the experimental value. The error in the calculated angle probably exceeds one degree being more like ±3–5 deg.

The geometry calculated for HClO can only be compared to that previously calculated using an *ab initio* CI method [8] as it has not been observed to date in the laboratory. The previous workers obtained Cl–O, 1.64 Å, Cl–H, 1.31 Å and a HClO angle of 104.4°. These are to be compared to our values of 1.723 Å, 1.272 Å, and 103.8° respectively. Since the two calculations employed a different basis set, we cannot expect complete agreement, but together they establish a structure with a H–Cl distance of 1.27–1.31 Å, a Cl–O distance of 1.64–1.72 Å, and a bond angle of about 104°. The H–Cl distance in HCl is known, to be 1.274 Å [22] while the Cl–O distance is known to be 1.470 Å [22], in ClO, 1.70 Å in Cl_2O [23], and 1.49 Å in ClO_2 [23]. Comparison of these results suggests a structure for HClO which contains a H–Cl single bond and a Cl–O bond which is very close to a single bond.

In Table II, we display the calculated total energies for HOCl, HClO, and the transition state obtained in

TABLE I. Calculated Molecular Geometries for HOCl and HClO

	HOCl			HClO	
	3-21G	6-31G(d)		3-21G	6-31G(d)
d O–H (Å)	0.9747	0.9512	*d* H–Cl (Å)	1.293	1.272
d Cl–O (Å)	1.767	1.670	*d* Cl–O (Å)	2.286	1.723
Angle (°)	104.3	105.1	Angle (°)	98.7	103.8
Dipole moment (Debye)	2.154	1.825		2.324	4.004

TABLE II. Calculated Total Energies[a]

	HOCl	HClO	Transition state
HF/6-31G(d)	−534.84197	−534.73316	−534.71061
HF/6-31G(d,p)	−534.84828	−534.73915	−534.71964
MP2/6-31G(d,p)	−535.16660	−535.04941	−535.02236
MP3/6-31G(d,p)	−535.18111	−535.06810	−535.03526
MP4(DQ)/6-31G(d,p)	−535.18333	−535.06985	−535.04555
MP4(SDQ)/6-31G(d,p)	−535.18543	−535.07387	−535.05319
MP4(SDTQ)/6-31G(d,p)	−535.19272	−535.08204	−535.06347

[a] Units: Hartree.

TABLE III. Correlation Energy Analysis

Calculation Level	HOCl	HClO	Transition State
MP2	0.31832	0.31026	0.30272
MP3	0.33238	0.32895	0.31562
MP4(DQ)	0.33505	0.33070	0.32591
MP4(SDQ)	0.33715	0.33472	0.33355
MP4(SDTQ)	0.34444	0.34289	0.34383
Estimated exact[a]	0.34490	0.34387	0.34535

[a] This estimate is obtained by taking the calculated fourth order correction to the energy, estimating the portion of the correlation energy remaining, and adding this portion to the calculated fourth order result. Units: Hartree.

passing from one valence isomer to the other. Table III shows the corresponding correlation energies. These results lead to a total energy of –535.19318 Hartree for HOCl, –535.08302 for HClO, and –535.06742 Hartree for the transition states. From the above results, we find an activation energy of 79 kcal/mol for the process of $HOCl \rightarrow HClO$ and an energy change of 70 kcal/mol. These same numbers calculated at the Hartree–Fock level are 81 kcal/mol and 65 kcal/mol respectively. The zero point energies of HOCl, HClO, and the transition state have been calculated to be 9.09, 6.16, and 4.09 kcal/mol respectively. These calculations were done using the 6-31G-(d) basis set. Incorporating the zero point energy differences into the above results leads to a best estimate of 67 kcal/mol for the energy of isomerization and 74 kcal/mol for the activation energy. The process is highly endothermic suggesting that the reaction of $ClO + HO_2$ to yield $HClO + O_2$ is probably not important in atmospheric chemistry. Our results can be compared to an estimate of 60 kcal/mol for the same energy difference by Bruna and coworkers [8]. We cannot make a similar comparison for our calculated activation energy as it has not been previously calculated. Bruna *et al.* have considered the system in an arbitrary geometry with a HOCl bond angle of 60° and commented that a 'small barrier might be present'. In the absence of an optimized geometry for the transition state, this represents an arbitrary point on the potential energy surface and is of little utility.

The Mulliken Population Analyses [24] of the three systems shows an H–O bond order of 0.293 in HOCl, 0.538 in HClO, but only 0.047 in the transition state illustrating the 'loose' bonding of the transition state. At first thought, the high O–H bond order in HClO might be interpreted that the molecule best be thought of as O–H–Cl rather than H–Cl–O (the H–Cl bond order is 0.226 while the Cl–O bond order is only 0.008) but this would be erroneous. The small Cl–O bond order is strictly due to the presence of the diffuse polarization 'd' type orbitals on the chlorine atom in the basis set. The failure of this population type of analysis is well known when applied to calculations which make use of extended basis sets [25].

In Table IV, we show the vibrational frequencies calculated for each isomer using the 6-31G(d) basis set. As usual, the calculated frequencies are about 10% too large [25]. Upon scaling the lowest frequency, ν_1, to force agreement with experiment the two remaining frequencies improve in agreement with experiment. Table IV also shows the calculated rotational constants for HOCl and HClO. These constants are presently available for only HOCl where the agreement with experiment is excellent. This is a

TABLE IV. Molecule Constants and Vibrational Frequencies

	HOCl		HClO	
	Calculated	Experimental[a]	Calculated	Experimental
1. Rotational constants (Ghz)				
A	645.0	613.4	342.9	–
B	15.51	15.16	15.17	–
	15.15	14.76	14.53	–

2. Vibrational frequencies (cm^{-1})

	HOCl			HClO
	Calculated	Scaled[c]	Experimental	Calculated
ν_1	854	724	724	326
ν_2	1424	1207	1240	858
ν_3	4078	3457	3609	3123

[a] Ref. 9. [b] Ref. 10. [c] The scale factor was selected so as to force agreement with experiment for ν_1 and then uniformly applied.

TABLE V. Ionization Potential Data for HOCl and HClO

HOCl			HClO	
	Calculated[a]	Experimental[b]		Calculated[a]
3a″	11.93	11.22	3a″	11.56
11a′	12.65	12.27	11a′	12.30
10a′	16.41	14.6	10a′	15.24
2a″	16.66	15.6	2a″	15.82
9a′	19.69	–	9a′	19.30

[a]Taken from a HF/6-31G(d,p) calculation. [b]Ref. 26.

direct reflection of the calculated geometry being in close agreement with the real molecular geometry.

In Table V we show the calculated ionization potentials for HClO and HOCl. Again only experimental data is available for HOCl [26], and we include it for comparison. The extent of agreement with photoelectron spectral results is reasonable. The first two spectral bands agree reasonably well with the calculated ionization potentials. Since we are using Koopman's theorem [27], we essentially have a measure of the extent to which the 6-31G(d,p) wave function is approaching the 'true' Hartree–Fock limit. The HONO orbital, 3a″ (antibonding), is composed entirely of the out of plane 'p' orbitals of chlorine and oxygen; for this orbital agreement is quite good. As we proceed down in energy to the inner molecular orbitals, agreement becomes poorer. For example, if we consider 2a″ orbital – a bonding orbital composed of out of plane atomic orbitals – the agreement appears much poorer in an absolute sense, but on a relative basis, it is in fact about the same, *i.e.*, the calculated orbital energy is about six percent too small in magnitude. Orbital 11a′ is a nonbonding lone pair orbital on chlorine; orbital 10a′ is a Cl–O bonding orbital, while 9a′ is an oxygen lone pair type orbital.

In the absence of experimental data, we shall not discuss the calculated I.P. values for HClO, but we simply present them as such.

Conclusion

The salient features of the valence isomerization process are shown in the Fig. 1. HClO lies some 67 kcal/mol above ground state HOCl. A barrier of 74 kcal/mol must be overcome in order to access ground state HClO from HOCl. The calculations have been carried out at the MP4SDTQ level of perturbation theory. Previous MP4SDTQ studies in HONO, a larger molecule than HOCl, exhibit an error in the energy of about 5 kcal/mol at this same level of calculation [28]. Since energy differences are dealt with in this work, some cancellation of error is to be expected.

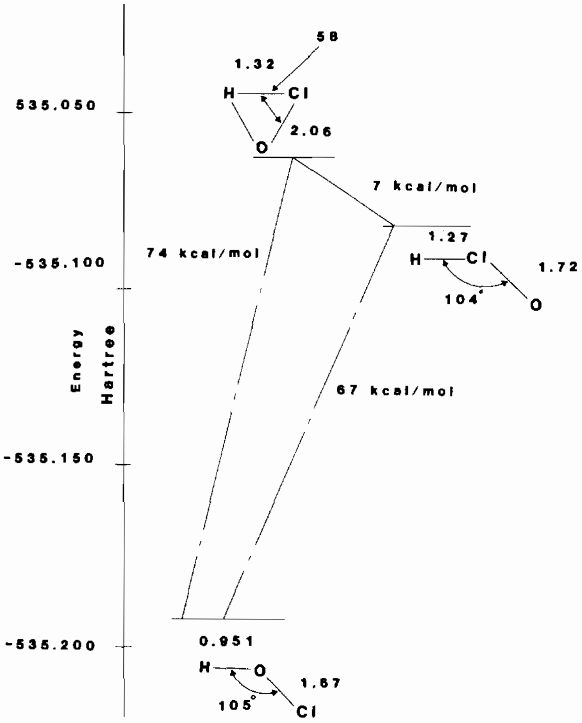

Fig. 1. The valence isomerization of HOCl ($^1A'$) → HClO ($^1A'$).

Nevertheless, we liberally estimate the results to be accurate to ±5 kcal/mol and thus suggest that

$$HOCl(g) \longrightarrow HClO(g)$$

$$\Delta H = 67 \pm\delta \text{ kcal/mol}$$

with an activation energy of 74 ± 5 kcal/mol.

Acknowledgements

The author wishes to recognize the National Research Council; National Academy of Sciences; and the Office of Scientific Research, U.S. Air Force, for the award of a NASA, National Research Council Associateship. He also wishes to thank the staff of the Frank J. Seiler Research Laboratory, U.S. Air Force Academy, for the hospitality provided to him. The expert typing of Mrs. Deborah Landess is acknowledged.

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