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An *Ab Initio* Study of *cis/trans* Isomerization in the XONO Systems (X = F, Cl)

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Abstract

Hartree–Fock level and post Hartree–Fock level molecular orbital calculations are reported for the *cis* and *trans* isomers of the FONO and ClONO molecules in their electronic ground states and for the transition states which are associated with their isomerization from the *cis* to *trans* forms.

Geometries have been determined together with respective vibrational frequencies, and the energy barrier for the isomerization reaction calculated. The barrier was found to be 67 kJ/mol for FONO and 67 kJ/mol for ClONO. The calculated isomerization energies are 16 kJ/mol and 20 kJ/mol respectively. We also report certain spectroscopic properties for the molecules.

Introduction

The ClONO molecule is of interest to the atmospheric chemist, and gas phase kineticist for many reasons. The molecule is one of several that may be formed from nitrogen dioxide and chlorine containing species and thus may have an active role in the coupling that is believed to occur in the ClO_x and NO_x cycles as they relate to the problem of stratospheric ozone depletion [1, 2]. The molecule is also of interest to the inorganic chemist as it represents an alternative structure to the $ClNO_2$ molecule [3].

Although the ClNO and FNO molecules have been studied in some detail [4, 5]*, relatively little is known about the FONO and ClONO systems. No previous theoretical studies have been reported. This laboratory has previously reported *ab initio* molecular orbital studies for a number of *cis–trans* systems and in this paper we continue these reports. Below we report a study of the geometries of the *cis* and *trans* forms of the FONO and ClONO molecules together with the geometries of the respective transition states for the two isomerization reactions. We also report a vibrational analysis for each molecule. We focus upon the energetics of the isomerization process and discuss the role of the basis set in the calculation of same.

Calculations

The calculations reported herein are of two types, Hartree–Fock Self Consistent Field type [6, 7] and Perturbative type employing the Moller–Plesset formulas [8, 9]. All the calculations were carried out using the Gaussian 82 computer program [10] and were carried out on a VAX 8600 or Cray XMP/48 computer. The reported geometries were optimized at the HF/6-31G(d) level and utilized the Berny minimization algorithm. Transition states were located by a calculation of all force constants and a maximization of the energy. All minima and transition states were confirmed by a vibrational analysis and an examination of the eigenvalues of the force constant matrix**. Post Hartree–Fock were carried out through fourth order including all contributions from the triple substitutions [11] and were performed using the HF/6-31G(d) geometry. The frozen core approximation was used†. The FG matrix method was utilized to perform the vibrational analysis [12]. The basis sets employed all contained polarization functions except the 3-21G set, the largest basis set being the 6-311++G(d) set [13–15]. It is well known that the use of a polarized basis set is necessary for molecules containing second and third atoms in order to

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*Reference 4 contains a number of references pointing out salient experimental and theoretical studies in the NOF system.

**The transition states calculated were confirmed by the occurrence of one and only one negative eigenvalue for the force constant matrix.

†In the frozen core approximation the contributions from the inner shell electrons are omitted in the calculation of the corrections to the energy. This has the effect of moving the energy up on the energy scale but the displacement cancels out upon subtraction of two energies and leads to little if any error in the calculated energy differences.

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TABLE I. Calculated Geometries for the XONO Systems

Species	Geometry					
	Distance (A)			Angles (°)		
	N=O	N–O	X–O	ONO	XON	Dihedral
NOFO						
cis	1.155	1.515	1.430	113.1	106.8	180.0
	1.142	1.365	1.363	115.8	111.1	180.0
trans	1.158	1.528	1.429	107.9	100.0	174.6
	1.144	1.380	1.429	108.8	104.5	180.0
Transition state	1.150	1.582	1.440	109.2	99.4	99.4
	1.133	1.464	1.371	119.8	101.9	101.9
NOClO						
cis	1.163	1.467	1.759	115.0	115.4	180.0
	1.144	1.359	1.679	116.5	117.5	180.0
trans	1.160	1.508	1.749	107.7	108.2	180.0
	1.143	1.389	1.655	109.0	110.4	180.0
Transition state	1.156	1.542	1.764	109.0	107.8	99.4
	1.136	1.443	1.670	111.0	110.1	110.1

Two geometries are listed for each entry, the first is the HF/3-21G optimized geometry and the second the HF/6-31G(d) optimized geometry.

obtain a reliable geometry [16]. Although the FONO and ClONO molecules are not normally considered to be hypervalent molecules*, we cannot be a priori certain that this will be true for the transition states considered herein. This makes it even more important to use a polarized basis set.

Results and Discussion

Geometries and Electronic Structure

The geometries calculated for the *cis* and *trans* forms of FONO and ClONO and the two transition states are shown in Table I. Two geometries are displayed, the first was calculated using the Hartree–Fock method and a 3-21G basis set, the second is that obtained from the same method and a 6-31G(d) basis set. Significant differences exist between the two geometries. In all the isomers the use of the larger basis set results in smaller bond distances, with the effect being most pronounced in the single bond distances. For example in FONO, both *cis* and *trans* forms, the halogen–oxygen distances and the nitrogen–terminal oxygen distances are shorter by about 0.08–0.14 Å. The same effect is present in the ClONO calculations. This is another illustration of the large error that can be present in the geometries calculated using self consistent field models and relatively small basis sets.

The bond distances and bond angles calculated are in reasonable accord with the same distances in similar molecules. For example the F–O single bond distance in the OF_2 molecule is 1.413 Å to be compared with our calculated distance of 1.36 Å [17]. A nitrogen oxygen double bond distance is normally considered to be around 1.15 Å [18] and can be compared to our calculated distance of 1.14 Å. A nitrogen oxygen single bond distance is generally taken to be 1.46 Å [19] and can be compared to our calculated distance of 1.36 Å in the *cis* form and 1.38 Å in the *trans* form. All the distances calculated seem to be uniformly shorter than the experimental results quoted giving credence to the suggestion that these molecules probably contain bonds which possess some small amount of multiple bond character.

The geometry calculated for the transition states does not differ in skeletal structure from that of the isomers themselves. It simply seems to be a question of the halogen atom rotating up out of the plane of the other three atoms with the energy rising in a continuous fashion and then passing through its maximum and falling again. The barrier is reasonably symmetric with its maxima displaced from the idealized 90° by about 2.5°.

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*By this remark we mean that the normal valence shell of the atoms does not have to be extended beyond those orbitals necessary to accommodate the usual octet of eight electrons.

TABLE II. Energetics for Isomerization Processes in ONOX Systems. Energies in Hartree, Enthalpies in kJ/mol

System – Calculation	E (cis)	E (*trans*)	E (TS)	ΔH	$\Delta H^{\#}$
ONOF					
HF/3-21G	−301.676322	−301.674060	−301.662539	5.9	36.2
HF/6-31G(d)	−303.355419	−303.353446	−303.334091	5.2	56.0
MP2/6-31G(d)	−304.054891	−304.048856	−304.029014	15.8	68.0
MP4SDQ/6-31G(d)	−304.063882	−304.059249	−304.040453	12.2	62.3
MP4SDTQ/6-31G(d)	−304.092770	−304.086649	−304.067092	16.0	67.4
ONOCl					
HF/3-21G	−660.126295	−660.120569	−660.111835	15.0	38.0
HF/6-31G*	−663.467285	−663.463531	−663.448867	9.9	48.4
MP2/6-31G*	−664.128167	−664.120425	−664.102832	20.3	66.5
MP4SDQ/6-31G(d)	−664.144168	−664.138125	−664.121251	15.8	60.1
MP4SDTQ/6-31G(d)	−664.173053	−664.165371	−664.147334	20.2	67.5

TABLE III. Correlation Energies – ONOX Systems

Calculation	*cis*	*trans*	Transition state
ONOF			
MP2/6-31G(d)	699	695	695
MP3/6-31G(d)	698	687	689
MP4SDTQ/6-31G(d)	737	733	733
ONOCl			
MP2/6-31G(d)	661	657	654
MP3/6-31G(d)	658	657	657
MP4SDTQ/6-31G(d)	708	702	698

Units: millihartree.

Energetics

The calculation of the energy of the barrier to *cis–trans* isomerization shows some surprising results. The results of our energy calculations are shown in Table II. It has been our experience that calculations of activation energies which employ small basis sets tend to over estimate the barrier [20]. This does not seem to be the case for these molecules. The lowest barriers are calculated from the 3-21G basis set. As the basis set is enlarged and the order of Perturbation Theory increased the calculated barrier increases. It is interesting to examine the correlation energy. One might anticipate that there should be a large degree of cancellation in the correlation energy upon calculation of the energy difference between the two isomers or an isomer and the transition state because the species are isoelectronic and of similar chemical structure. This frequently occurs. In Table III we show the correlation energies of the molecules and the transition states. The correlation energies are relatively constant differing between the *cis* and *trans* isomers by only 10 kJ/mol. The difference in the correlation energy of the transition state and the appropriate *cis* isomer is also very small, *i.e.* less than 2 kJ/mol for the FONO system and 20 kJ/mol for the ClONO system. These are relatively small differences and certainly are within the error of the calculations. They are principally due to our use of the frozen core approximation wherein we have made no attempt to introduce the correlation effects of the inner shell electrons. We have included a correction for the difference in zero point vibrational energy of the reactant and product and thus the respective activation energies for the *cis–trans* processes are 67 kJ/mol for FONO and 67 kJ/mol for the ClONO system. The respective energies of isomerization are 16.0 kJ/mol and 20 kJ/mol with the *cis* form being the lower energy isomer. We estimate the error in these results to be plus or minus 10 kJ/mol. The error is traceable to our use of the limited basis set which in turn limits the calculation of the fourth order correction to the energy. From Table II one can readily note the effect of and importance of the inclusion of the contributions of the 'triple' substitutions to the fourth order energy. The calculated energy changes increase by about 5 kJ/mol when these terms are included. It should also be noted that the results obtained using the minimal 3-21G basis set differ substantially from the more reliable result obtained with the larger basis set.

Spectroscopic Properties

Tables IV and V display the calculated vibrational frequencies and rotational constant for the FONO and ClONO molecules. The vibrational results have been calculated using the 6-31G(d) basis set at the Hartree–Fock geometry. As such they are expected to be about ten percent too large and should be scaled accordingly. We also include in the Table the

TABLE IV. Calculated Vibrational Frequencies, HF/6-31G(d) (cm^{-1})

	cis	*trans*	Transition state
FONO	382	232	-231
	397	446	398
	854	674	682
	950	1027	902
	1215	1250	1170
	2051	2068	2085
Zero point *E* (kJ/mol)	34.99	34.08	31.32
ClONO	312	181	-209
	360	349	315
	758	587	684
	865	938	849
	1030	1035	919
	2028	2065	2068
Zero point *E* (kJ/mol)	32.02	30.84	28.92

TABLE V. Calculated Rotational Constants, HF/6-31G(d) (GHz)

	cis	*trans*	Transition state
FONO			
A	23.61	64.69	28.37
B	8.043	5.313	6.342
C	5.999	4.910	5.730
ClONO			
A	19.95	62.18	24.57
B	4.683	3.204	3.882
C	3.793	3.049	3.558

zero point energies calculated for each isomer of each molecule. The *cis* and *trans* isomers of FONO have about the same zero point energy, namely, 34 kJ/mol. The ClONO molecule in the *cis* form has a zero point energy which is 2 kJ/mol larger than that of the *trans* form. Both isomers of each molecule have zero point energies which are larger than those of the corresponding transition state reflecting the fact that they are 'more tightly' bonded in the *cis* and *trans* forms than they are in the transition state. This is also reflected in the calculated bond orders in the population analysis, and the calculated bond distances for each species.

The vibrational frequencies calculated for the *cis* isomer are generally larger than those for the *trans* with the exception of the second and fourth frequencies which are associated with collective motions which involve the halogen atom and the ONO skeletal frame.

Table V contains the calculated rotational constants for the four isomers and one notes that the constants for the respective *cis* and *trans* isomer pairs differ significantly enough that they should be spectroscopically distinguishable. In particular the B and C constants are appreciably larger for the *cis* forms and, as expected, the A constant is much larger for the *trans* isomer.

Finally one point should be noted. The *cis* and *trans* isomers for FONO and ClONO have a higher energy than the C_{2v} form of each molecule wherein the skeletal structure is of the type X–NO_2 with each oxygen atom located symmetrically with reference to the X–N bond axis. The relative stability of the isomers with respect to this C_{2v} form is the subject of another communication.

Conclusions

The *cis* forms of both FONO and ClONO are energetically favored over the *trans* forms with a activation energy of 67 kJ/mol required for their interconversions. The isomers can be expected to differ enough in geometry to be easily distinguished spectroscopically.

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