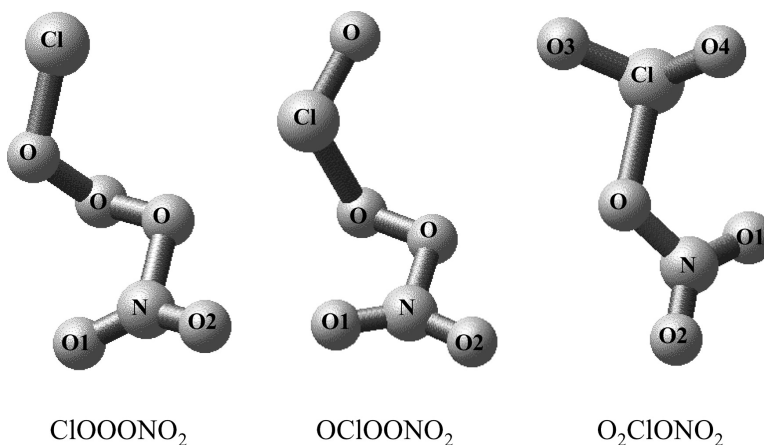


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Theoretical Study of Chlorine Nitrates: Implications for Stratospheric Chlorine Chemistry

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Abstract: Reported here is a theoretical study of possible stratospheric chlorine reservoir species including isomers of chemical formula ClNO₄ and ClNO₅, in addition to the well-known ClONO₂ reservoir species. Density functional theory (DFT) in conjunction with large one-particle basis sets has been used to determine equilibrium structures, dipole moments, rotational constants, harmonic vibrational frequencies, and infrared intensities. The B3LYP functional was used since it has previously been shown to perform well for similar compounds. The equilibrium geometry and vibrational spectra of ClONO₂ are shown to be in good agreement with the experimental data and also with high-level coupled-cluster calculations reported previously. Three stable isomers have been identified for each ClNO₄ and ClNO₅. The vibrational spectrum of O₂ClONO₂ has been compared with the available experimental data and found to be in good agreement. The relative energetics of the ClNO₄ and ClNO₅ isomers have been determined using large atomic natural orbital (ANO) basis sets in conjunction with the singles and doubles coupled-cluster method that includes a perturbational correction for triple excitations, denoted CCSD(T). Accurate heats of formation have been evaluated by computing energies for isodesmic reactions involving the ClNO₄ and ClNO₅ isomers. The stability of these molecules with respect to thermal dissociation is examined. The present study suggests that isomers of ClNO₄ and ClNO₅ may have no atmospheric chemical relevance because the atmospheric concentrations of the necessary reactants are insufficient, but it is also found that under laboratory conditions the formation of O₂ClONO₂ cannot be ignored.

Introduction

It has been known for a number of years that high levels of chlorine radicals (ClO_x) observed¹⁻³ in the polar stratosphere couple with nitrogen oxides (NO_x) resulting in the removal of reactive chlorine species by conversion into temporary reservoir species. Of the various possible reactions between the ClO_x and NO_x families, the association reaction between ClO and NO₂ to produce chlorine nitrate, ClONO₂, has been considered the most significant:



The suggestion that ClONO₂ could be an important reservoir species was first made by Rowland *et al.*⁴ in 1976. Since then, a significant effort has been expended in elucidating the chemistry of ClONO₂ in the stratosphere, including its hetero-

geneous chemistry (see ref 5 and references therein). Also, a large number of field measurements have been made to ascertain the abundance of ClONO₂ in the chemically perturbed region of the polar vortex (see ref 6 and references therein).

Despite the enormous work, there are still discrepancies, on the order of 5% depending on latitude and altitude, in balancing the atmospheric chlorine budget.^{7,8} Researchers believe that additional long-time chlorine reservoir species may be involved besides the currently recognized chlorine reservoirs, ClONO₂ and HCl. Attempts to improve the current understanding have led to the conclusion^{9,10} that higher oxides of chlorine heretofore overlooked may account for the missing reservoir of inorganic chlorine in the stratosphere. This speculation arose partly from the ground based measurements that detected¹¹ extraordinarily

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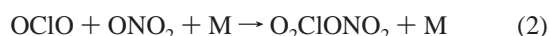
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high concentrations of OCIO in the polar vortex, which is believed to be produced primarily by the coupling between ClO and BrO. Apart from OCIO, significant stratospheric column abundances of NO₃ have been observed¹² in early December and February in the Arctic and in September in the Antarctic. The observation of OCIO and NO₃ in the polar stratosphere has strengthened the notion that many more reactions are possible between the NO_x and ClO_x families. In response to these findings, some effort has been directed at the alternative possibility of gas-phase reservoir species resulting from the reactions of OCIO with NO₃ and ClO with NO₃.

Friedl *et al.*¹³ examined the products of the reaction between OCIO and NO₃ from $T = 220$ to 298 K using a flow reactor and infrared, visible, and ultraviolet spectroscopic analysis. Further, IR and UV absorption features observed at low temperature (<230 K) were assigned to the novel compound chloryl nitrate, O₂ClONO₂.



Using a one-dimensional model, they deduced that chloryl nitrate may exist in significant concentrations in the “collar” region of the polar vortex, where both the reactants are likely to exist in the nighttime air mass. However, in a later study, Boyd *et al.*¹⁴ found no evidence for the occurrence of the homogeneous reaction NO₃ + OCIO → products at room temperature, in disagreement with Friedl *et al.*¹³ It is noteworthy that the existence of chloryl nitrate, O₂ClONO₂, was first suggested by Christe *et al.*¹⁵ as an unstable intermediate species for the reaction between FClO₂ and N₂O₅.

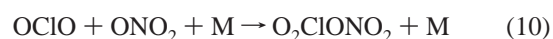
In the study of the reaction between ClO and NO₃, two channels were considered, viz



Several groups have studied this reaction, but its atmospheric importance has not been demonstrated. There is some disagreement as to the branching ratio. Cox *et al.*¹⁶ and Biggs *et al.*¹⁷ suggested that the ClOO forming channel was predominant, while the study by Becker *et al.*¹⁸ favored the formation of OCIO. Further, Biggs *et al.*¹⁷ reported a low rate constant for the reaction between NO₃ and ClO and suggested that the slowness of the reaction might be due to formation of an adduct or as a result of the reaction proceeding via a many-centered transition state.

In general, the higher oxides of chlorine nitrates could be important if they are produced in sufficient amounts to act as temporary or long-term reservoirs for both odd chlorine and odd nitrogen species. Further, independent of their atmospheric significance, the recombination products are interesting mol-

ecules from the viewpoint of structural chemistry. Therefore, it is important to establish the properties of these oxides to aid in the interpretation of laboratory and atmospheric observations. In the present study, we have considered the following reactions as the possible pathways for the adduct formation:



Finally, the possibility of coupling between OCIO₂ with NO_x should also be considered, although we note that there has been a debate on how strongly ClO₃ is bound and thus its significance to stratospheric chemistry (e.g., see refs 19–26):



To our knowledge, there have not been any high-level *ab initio* investigations of higher oxides of chlorine nitrates reported in the literature. Moreover, we are not aware of any experimental information for ClNO_x ($x = 4, 5$) except for the preliminary study on the O₂ClONO₂ species by Friedl *et al.*¹³ Therefore, the purpose of the present study is 2-fold. First and foremost, the purpose is to characterize the ClNO_x ($x = 3-5$) molecules, by determining their equilibrium geometries and vibrational spectra, and to determine the lowest energy isomer of ClNO_x ($x = 4, 5$) using quantum-chemical methods. In the present study, we have decided to use the B3LYP density functional theory (DFT) since it has been shown to yield reasonable geometrical structures and vibrational frequencies for other chlorine and bromine oxygen compounds (e.g., see refs 27–30 and references therein). Nonetheless, to assess better the performance of B3LYP/DFT for chlorine nitrates, we also benchmark the B3LYP results of ClONO₂ against high level coupled-cluster calculations,³¹ as well as experimental data,^{32–35} which have already been reported in the literature. The second purpose of this study is to predict accurately the thermochemical data that are not yet available from experiment. On the basis of experience,^{27–31} it is expected that the CCSD(T) method (singles and doubles coupled-cluster theory plus a perturbational estimate of the effects of connected

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triple excitations), in conjunction with large atomic natural orbital basis sets, will yield accurate heats of formation for the ClNO_x ($x = 3-5$) species. Thus, single-point energies were computed at the CCSD(T) level for the B3LYP geometries in order to study the relative energies and heats of formation. The theoretical approach is detailed in the next section, while our results and discussion are presented in the following section. The implications for stratospheric chlorine chemistry due to this study are then discussed, and conclusions are presented in the final section.

Computational Methods

Total energies, equilibrium geometries, dipole moment, harmonic frequencies and infrared (IR) intensities were determined for all the species using the B3LYP hybrid functional as implemented within the Gaussian 94 quantum chemistry program package.³⁶ The interested reader is referred to ref 37 and references therein for a complete description of the B3LYP functional. Four valence triple- ζ quality basis sets were used in this study. The first is the split-valence triple- ζ basis set augmented with two sets of d -polarization functions. This comprises the 6-311G(2d) basis set. Another set of polarization functions supplement the 6-311G(2d) basis set to comprise the 6-311G(3d) basis set. A set of f -polarization functions and a set of diffuse functions are also added to comprise the 6-311+G(3df) basis set. The fourth basis set used is a triple- ζ double-polarized (TZ2P) basis set composed of Dunning's³⁸ contraction of Huzinaga's³⁹ primitive set, for nitrogen and oxygen. These sp sets are supplemented with two sets of polarization functions ($\alpha_d = 2.314, 0.645$ for O and $1.654, 0.469$ for N). The chlorine TZ2P basis set is composed of McLean and Chandler's⁴⁰ [6s5p] contracted functions supplemented with two sets of polarization functions ($\alpha_d = 1.072, 0.357$).

To determine accurate heats of formation for ClOONO_2 , ClONO_2 , O_2ClNO_2 , ClOONO_2 , O_2ClONO_2 , isodesmic reaction energies have been evaluated at the SCF, MP2, CCSD, and CCSD(T) levels of theory using large atomic natural orbital (ANO) basis sets.⁴¹ Isodesmic reactions conserve numbers and types of bonds between reactants and products and are well-known to lead to a significant cancellation of errors in *ab initio* calculations in most cases. The ANO basis sets have been described in detail previously.^{41,42} The basis set denoted ANO2 consists of 5s4p2d1f and 4s3p2d1f ANOs on Cl and (N,O), respectively. For the ANO basis sets, only the spherical harmonic components of the d - and f -type functions were included. The B3LYP geometry optimizations were performed with the Gaussian 94 program,³⁶ while the single-point calculations were performed with the MOLPRO96 program.⁴³

Results and Discussion

A. Equilibrium Structures. Among the various chlorine nitrates considered in this study, ClNO_3 , resulting from the

Table 1. Total Energies (E_h), Equilibrium Structures, Rotational Constants (MHz), and Dipole Moments (D) of ClOONO_2^a

	6-311G(2d)	6-311G(3df)	6-311+G(3df)	TZ2P
E	0.692 36	0.706 33	0.723 60	0.731 64
μ	0.30	0.29	0.45	0.42
r_{ClO}	1.800	1.772	1.751	1.776
r_{OO}	1.340	1.345	1.351	1.353
r_{ON}	1.603	1.594	1.586	1.597
r_{NO_1}	1.180	1.178	1.178	1.180
r_{NO_2}	1.184	1.181	1.181	1.183
$\angle\text{ClOO}$	111.2	111.2	111.2	111.2
$\angle\text{OON}$	108.7	108.8	109.1	109.2
$\angle\text{ONO}_1$	114.7	114.7	115.0	115.1
$\angle\text{ONO}_2$	109.3	109.2	109.2	109.2
τClOON	91.0	91.2	91.5	91.5
τOONO_1	-2.5	-2.4	-1.6	-1.9
τOONO_2	177.2	177.3	178.1	177.8
A_e	7418	7514	7571	7484
B_e	1663	1678	1682	1658
C_e	1542	1556	1562	1540

^a The energy is reported as $-(E + 815)$. Bond lengths are in Å, and angles, in deg. See Figure 1 for labeling of atoms.

Table 2. Total Energies (E_h), Equilibrium Structures, Rotational Constants (MHz), and Dipole Moments (D) of ClONO_2^a

	6-311G(2d)	6-311G(3df)	6-311+G(3df)	TZ2P
E	0.657 83	0.676 67	0.704 47	0.700 94
μ	1.93	1.97	2.04	2.10
r_{OCl}	1.519	1.508	1.499	1.521
r_{ClO}	1.771	1.726	1.674	1.756
r_{ON}	1.506	1.533	1.584	1.523
r_{NO_1}	1.190	1.185	1.181	1.188
r_{NO_2}	1.189	1.184	1.179	1.186
$\angle\text{ClON}$	113.7	113.7	113.5	113.8
$\angle\text{ONO}_1$	117.4	116.7	115.7	117.0
$\angle\text{ONO}_2$	109.5	109.3	109.2	109.4
$\angle\text{OCIO}$	114.0	113.1	112.9	113.0
τClONO_1	2.0	3.5	5.7	3.3
τClONO_2	-180.0	-180.0	-180.0	-176.8
τOCION	85.3	85.4	86.1	85.5
A_e	8072	8028	7952	7988
B_e	1768	1800	1818	1772
C_e	1623	1655	1674	1633

^a The energy is reported as $-(E + 815)$. Bond lengths are in Å, and angles, in deg. See Figure 1 for labeling of atoms.

reaction of ClO with NO_2 , is the only molecule studied extensively both by experiment and theory. The reaction between ClO and NO_2 is now accepted to give a single product, ClONO_2 . Possible formation of chlorine peroxyxynitrite, ClOONO has been considered in the past,⁴⁴ but there is no compelling evidence supporting the existence of this isomer nor any other possible isomer of chlorine nitrate. Therefore, we have not considered other possible connectivities for the ClNO_3 molecule. On the other hand, we have studied a few possible isomers for ClNO_4 and ClNO_5 , because there is no definite structural information available yet on these species. The B3LYP structural parameters, dipole moments, rotational constants, and absolute energy values of six structures are presented in Tables 1–6. The fully optimized geometries for isomers of ClNO_4 and ClNO_5 are presented in Figures 1 and 2, respectively. The equilibrium structure of ClONO_2 has been studied theoretically previously, and thus, in order to minimize discussion involving the comparison of methods, the B3LYP optimized structure and structural parameters for ClONO_2 are presented as Supporting

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Table 3. Total Energies (E_h), Equilibrium Structures, Rotational Constants (MHz), and Dipole Moments (D) of $O_2CINO_2^a$

	6-311G(2d)	6-311G(2df)	6-311+G(3df)	TZ2P
E	0.645 31	0.668 47	0.699 98	0.685 53
μ				1.86
r_{ClO_3}	1.477	1.466	1.455	1.482
r_{ClO_4}	1.480	1.469	1.458	1.485
r_{ClN}	2.217	2.197	2.206	2.232
r_{NO_1}	1.195	1.192	1.192	1.193
r_{NO_2}	1.191	1.189	1.187	1.189
$\angle O_3CIN$	95.8	96.1	96.8	96.7
$\angle O_4CIN$	102.3	102.1	102.3	102.5
$\angle CINO_1$	116.5	116.3	116.1	116.0
$\angle CINO_2$	109.6	109.8	110.2	110.0
$\angle O_3ClO_4$	117.2	116.7	116.5	116.6
$\angle O_1NO_2$	133.9	133.8	133.7	134.0
τO_3CINO_1	180.0	179.7	173.8	176.7
τO_4CINO_1	-60.5	-61.3	-67.1	-64.1
τO_3CINO_2	-2.4	-2.5	-7.6	-5.0
τO_4CINO_2	117.2	116.5	111.5	114.1
A_e	5224	5287	5353	5225
B_e	2375	2405	2361	2324
C_e	1788	1814	1819	1774

^a The energy is reported as $-(E + 815)$. Bond lengths are in Å, and angles, in deg. See Figure 1 for labeling of atoms.

Table 4. Total Energies (E_h), Equilibrium Structures, Rotational Constants (MHz), and Dipole Moments (D) of $ClOOONO_2^a$

	6-311G(2d)	6-311G(2df)	6-311+G(3df)	TZ2P
E	0.855 82	0.872 15	0.892 26	0.902 77
μ	0.28	0.29	0.42	0.45
r_{ClO}	1.756	1.734	1.716	1.738
r_{OO}	1.414	1.420	1.427	1.428
r_{OO}	1.376	1.369	1.363	1.376
r_{ON}	1.569	1.572	1.577	1.576
r_{NO_1}	1.182	1.179	1.178	1.180
r_{NO_2}	1.185	1.182	1.181	1.183
$\angle ClOO$	110.0	110.1	110.2	110.1
$\angle OOO$	108.9	108.9	108.9	109.1
$\angle OON$	108.9	109.0	109.2	109.3
$\angle ONO_1$	115.6	115.4	115.4	115.7
$\angle ONO_2$	109.0	109.0	109.0	108.9
$\tau ClOOO$	82.8	82.5	82.6	83.0
τOON	83.4	83.9	85.0	85.0
$\tau OONO_1$	-1.5	-1.3	-0.2	-0.9
$\tau OONO_2$	178.3	178.5	179.4	178.8
A_e	6093	6120	6172	6156
B_e	1081	1088	1084	1069
C_e	1017	1023	1018	1004

^a The energy is reported as $-(E + 890)$. Bond lengths are in Å, and angles, in degrees. See Figure 2 for labeling of atoms.

Information in Figure S1 and Table S1, respectively. For later reference, we note that, in Figure S1, O refers to the oxygen bonded to the Cl and N atoms, while O1 and O2 refer to the oxygen atoms that are cis and trans relative to the Cl atom, respectively. The following discussion will focus on each molecule or set of molecules, in the order of $ClONO_2$, $CINO_4$ isomers, and $CINO_5$ isomers, followed by a brief discussion on the trends in chlorine/oxygen bonding in these compounds.

$ClONO_2$. A more detailed discussion of the $ClONO_2$ optimized structure is presented in the Supporting Information. Here we present only the salient details. The IR spectra³⁵ of gas-phase and matrix-isolated $ClONO_2$ and the experimental³² structural determination strongly support a planar structure and the closely related molecules $BrONO_2$,³² $HONO_2$,⁴⁵ and CH_3ONO_2 ⁴⁶ have already been established to be planar; therefore,

(45) Cox, A. P.; Riveros, J. M. *J. Chem. Phys.* **1965**, *42*, 3106.

Table 5. Total Energies (E_h), Equilibrium Structures, Rotational Constants (MHz), and Dipole Moments (D) of $OCIOONO_2^a$

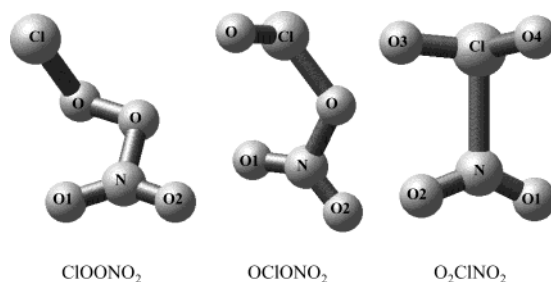
	6-311G(2d)	6-311G(2df)	6-311+G(3df)	TZ2P
E	0.824 27	0.843 53	0.872 14	0.874 21
μ	1.74	1.74	1.78	1.92
r_{OCl}	1.530	1.515	1.504	1.531
r_{ClO}	1.925	1.870	1.834	1.918
r_{OO}	1.335	1.348	1.353	1.337
r_{ON}	1.591	1.574	1.571	1.601
r_{NO_1}	1.185	1.183	1.181	1.182
r_{NO_2}	1.184	1.182	1.181	1.182
$\angle OCIO$	114.1	113.3	112.8	113.0
$\angle ClOO$	111.9	111.8	111.8	112.0
$\angle OON$	109.2	109.4	109.5	109.6
$\angle ONO_1$	114.8	115.1	115.2	114.8
$\angle ONO_2$	109.9	109.7	109.5	109.7
$\tau OCIOO$	77.8	78.7	79.0	74.8
$\tau ClOON$	87.8	88.0	89.5	89.5
$\tau OONO_1$	-7.6	-7.9	-7.0	-6.8
$\tau OONO_2$	172.7	172.5	173.3	173.4
A_e	5799	5941	6043	5749
B_e	1134	1159	1167	1130
C_e	1075	1095	1099	1070

^a The energy is reported as $-(E + 890)$. Bond lengths are in Å, and angles, in deg. See Figure 2 for labeling of atoms.

Table 6. Total Energies (E_h), Equilibrium Structures, Rotational Constants (MHz), and Dipole Moments (D) of $O_2CINO_2^a$

	6-311G(2d)	6-311G(2df)	6-311+G(3df)	TZ2P
E	0.833 00	0.859 99	0.894 02	0.878 75
μ	2.35	2.26	2.36	2.49
r_{ClO}	1.978	1.942	1.937	1.983
r_{ON}	1.387	1.391	1.392	1.389
r_{NO_1}	1.214	1.210	1.209	1.211
r_{NO_2}	1.200	1.196	1.196	1.199
r_{ClO_3}	1.452	1.442	1.433	1.457
r_{ClO_4}	1.450	1.441	1.431	1.455
$\angle ClON$	110.8	111.5	112.8	112.4
$\angle ONO_1$	117.3	117.0	117.0	117.3
$\angle ONO_2$	113.3	113.2	113.2	113.2
$\angle O_3ClO$	98.0	97.6	97.1	97.8
$\angle O_4ClO$	103.9	103.5	103.5	103.7
$\tau ClONO_1$	3.4	4.2	5.2	4.1
$\tau ClONO_2$	177.1	176.3	175.4	176.4
τO_3ClON	164.0	165.2	166.8	164.8
τO_4ClON	-77.4	-76.7	-75.0	-76.9
A_e	5620	5671	5694	5587
B_e	1440	1462	1460	1419
C_e	1271	1290	1286	1254

^a The energy is reported as $-(E + 890)$. Bond lengths are in Å, and angles, in deg. See Figure 2 for labeling of atoms.

**Figure 1.** Atom numberings of the three isomers of $CINO_4$ isomers.

we have only considered planar conformations for $ClONO_2$. At the B3LYP/TZ2P level, our calculated structure is in very good agreement with experiment. The difference between B3LYP/TZ2P bond distances and the experimental values are ~ 0.01 –

(46) Cox, A. P.; Waring, S. *Trans. Faraday Soc.* **1971**, *67*, 3441.

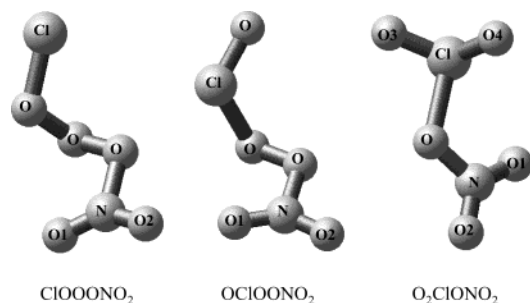


Figure 2. Atom numberings of the three isomers of ClNO_5 isomers.

0.03 Å, while the calculated bond angles differ by 0.2°, 1.1°, and 0.2° from the experimental values for the ClON , ONO_1 , and ONO_2 angles, respectively. Agreement between the B3LYP/TZ2P and the recently published³¹ CCSD(T)/TZ2P geometrical parameters for ClONO_2 is also good. Based on the excellent agreement between experiment and the B3LYP results, there is every reason to expect reliable results for the other chlorine nitrates included in this study.

ClNO_4 Isomers. For ClNO_4 , we have examined three isomeric forms viz, ClOONO_2 , OCIONO_2 , and O_2ClNO_2 using the 6-311G(2d), 6-311G(2df), 6-311+G(3df), and TZ2P basis sets in conjunction with the B3LYP approach. The equilibrium geometries are given in Tables 1–3, respectively, and illustrated in Figure 1. From the computations, the minimum-energy structure for ClOONO_2 appears to be skewed. The ClOON dihedral angle at the B3LYP/TZ2P level of theory is predicted to be 91.5°. Note that B3LYP/6-311+G(3df) predicts the same value. The structures obtained with different basis sets exhibit relatively small differences, which mostly concern the bond lengths. Upon improving the basis set from 6-311G(2d) to 6-311+G(3df), we observed the Cl–O distance decreases by 0.049 Å and the central O–N bond distance decreases by 0.017 Å, whereas the O–O bond lengthens by 0.011 Å. The bond angles do not exhibit significant changes due to improvements in the basis set. In fact, the ClOO bond angle (111.2°) is insensitive to the basis set, and it is predicted to be slightly larger than the OON bond angle. The large ClOO angle is likely due to the repulsion between the three lone pairs of electrons on chlorine and its neighbors.

The second isomeric form we considered is OCIONO_2 (Table 2). The OCION dihedral angle is 85.5° at the B3LYP/TZ2P level of theory. Refer to Figure 1 for the labeling of atoms. The basis-set effects on the Cl–O bond distances are similar to those observed for ClONO_2 and ClOONO_2 , but the central Cl–O bond length in OCIONO_2 is more sensitive to basis set. At the B3LYP/6-311G(2d) level the central Cl–O and terminal Cl–O bond distances are 1.771 Å and 1.519 Å, respectively. The addition of f -functions to the oxygen and chlorine reduces the central Cl–O bond length by 0.045 Å and terminal Cl–O bond length by 0.011 Å. When another set of d - and f -polarization functions are added to the atoms and supplemented by diffuse functions, the central Cl–O bond length shortened by 0.052 Å, while the terminal Cl–O bond length decreased by only 0.009 Å. It is noteworthy that the central N–O bond length varies by as much 0.078 Å among the basis sets with 6-311G(2d) predicting the shortest central N–O bond and 6-311+G(3df) predicting the longest central N–O bond distance. The other structural parameters are not greatly influenced by basis set enlargement.

The atom numberings for the third isomeric form, O_2ClNO_2 , are listed in Figure 1, and the optimized geometries are listed in Table 3. The Cl–N bond length in O_2ClNO_2 varies as much as 0.035 Å among the basis sets, with TZ2P predicting the longest Cl–N bond distance (2.232 Å). The only significant observation concerning the basis set effects is the decreasing trend in terminal Cl–O bond lengths with the improvements in basis sets. It is perhaps more interesting to compare the trends that arise from various basis sets for Cl–O bond lengths with similar molecules, such as HOClO_2 and ClClO_2 . For the former, Francisco and Sander⁴⁷ showed that at the MP2 level the Cl–O bond length decreased from 1.466 Å (6-31G(d)) to 1.452 Å (6-311G(2d,2p)) to 1.440 Å (6-311G(2df,2p)). For ClClO_2 , Lee *et al.*⁴⁸ showed that at the MP2 level the Cl–O bond length decreased from 1.477 Å (DZP) to 1.451 Å (TZ2P) to 1.442 Å (TZ2PF). We observe a similar convergence for O_2ClNO_2 . That is, the Cl–O terminal bonds decrease from 1.477 and 1.480 Å (6-311G(2d)) to 1.466 and 1.469 Å (6-311G(2df)) to 1.455 and 1.458 Å (6-311G(3df)). It is noteworthy that the terminal Cl–O bonds in both OCIONO_2 and O_2ClNO_2 are shorter than the normal Cl–O single bonds. This is due to an increase in the ionic component to bonding on going from $\text{ClOONO}_2 < \text{OCIONO}_2 < \text{O}_2\text{ClNO}_2$ and an increase in the hypervalent nature of the chlorine atom due to $p \rightarrow d$ promotion, giving the terminal Cl–O linkages some double bond character.⁴⁹

ClNO_5 Isomers. Similar to the ClNO_4 isomers, calculations were carried out for ClNO_5 isomers in order to identify the lowest energy isomer on the hypersurface of the ClNO_5 potential energy. The geometrical parameters for the three isomers ClOONO_2 , OCIOONO_2 , and O_2ClNO_2 (see Figure 2) calculated using the B3LYP method in conjunction with the 6-311G(2d), 6-311G(2df), 6-311+G(3df), and TZ2P basis sets are listed in Tables 4–6, respectively. Computations indicate that the minimum-energy structure for ClOONO_2 is skewed. The ClOOO dihedral angle at the B3LYP/TZ2P level of theory is 83.0°, and the OON dihedral angle is predicted to be 85.0°. Examination of the *ab initio* equilibrium structures in Table 4 shows a decreasing trend in the Cl–O bond length with increased size of the basis set. The difference between the 6-311G(2d) and 6-311+G(3df) Cl–O bond length is 0.040 Å. The OOO and OON bond angles are almost the same but shorter than the ClOO bond angle. As mentioned earlier, the wide angle of ClOO is mainly due to the repulsion between the three lone pairs of electrons on chlorine and its surrounding neighbors. It is noteworthy that the bond and torsion angles obtained via the four basis sets are similar, showing only slight variations (on the order of tenths of degrees). Comparison of the peroxide bonding in ClOONO_2 with that of ClOONO_2 indicates that the O–O bond lengths in ClOONO_2 are longer than the O–O bond in ClOONO_2 . The O–O bond linked to nitrogen is closer to the O–O bond in ClOONO_2 than the O–O bond connected to the chlorine. The striking difference between ClOONO_2 and ClOONO_2 is that the central O–N bond distance increases with the improvements in basis set for ClOONO_2 , while ClOONO_2 exhibits a decreasing trend.

The second isomeric form we considered is a nonplanar skew structure OCIOONO_2 with the oxygen as the terminal atom. The results are listed in Table 5 and illustrated in Figure 2. At

(47) Francisco, J. S.; Sander, S. P. *J. Phys. Chem.* **1996**, *100*, 573.

(48) Lee, T. J.; Rohlfing, C. M.; Rice, J. E. *J. Chem. Phys.* **1992**, *97*, 6593.

(49) Lee, T. J.; Dateo, C. E.; Rice, J. E. *Mol. Phys.* **1999**, *96*, 633.

the B3LYP/TZ2P level of theory, the dihedral angle between the ClOO atoms is 74.8° , while that between ClOON is 89.5° . At the B3LYP/6-311G(2d) level of theory, the central Cl–O and terminal Cl–O bond distances are 1.925 Å and 1.530 Å, respectively. The addition of *f*-functions to the oxygen and chlorine reduces the central Cl–O bond length by 0.055 Å and the terminal Cl–O bond length by 0.015 Å. When another set of *d*- and *f*-polarization functions are added to the atoms and supplemented by diffuse functions, the central Cl–O bond length is reduced by a further 0.036 Å and the terminal Cl–O bond by a further 0.011 Å. It is also noteworthy that the central N–O bond length decreased from 1.591 Å (6-311G(2d)) to 1.574 Å (6-311G(2df)) to 1.571 Å (6-311+G(3df)). Other structural parameters do not exhibit large changes due to improvements in the basis sets. Overall, the geometries are fairly similar to that of ClOONO₂.

Finally, we considered the isomeric form O₂ClONO₂. The atom numberings for O₂ClONO₂ are given in Figure 2, and the optimized geometries are listed in Table 6. The geometries obtained via the four basis sets are all similar showing only slight variations in bond length and angles, on the order of hundredths of angstroms and tenths of degrees. The most significant change with respect to basis set is the central Cl–O bond length, which varies as much as 0.046 Å among the basis sets, with TZ2P predicting the longest central Cl–O bond. Similar to the central Cl–O bond, the terminal Cl–O bonds also show systematic shortening of bond lengths from 6-311G(2d) to 6-311+G(3df), but the change is not as appreciable as that of the central Cl–O bond. From Table 6, note that the predicted terminal Cl–O bond lengths are shorter than the central Cl–O bond with all four basis sets. As previously mentioned, this can be attributed to increased ionic and hypervalent character associated with the terminal Cl–O bonds. It is important to note that the ionic and hypervalent characters are more pronounced in O₂ClONO₂ relative to ClOONO₂, making the Cl=O double bond character more pronounced in O₂ClONO₂ compared to ClOONO₂. Thus, the terminal Cl–O bond distances for O₂ClONO₂ (1.457 and 1.455 Å with the TZ2P basis set) are smaller than the terminal Cl–O bond distance of 1.521 Å in ClOONO₂. A similar trend was observed by Lee *et al.*⁴⁹ for several chlorine/oxygen and bromine/oxygen single and double bonds examined for several molecules of interest in stratospheric halogen chemistry. For example, Lee *et al.*⁴⁸ calculated Cl–O bond distances at the CCSD(T)/TZ2P level of theory for Cl₂O₂ isomers and reported 1.753 and 1.468 Å for ClOOCl and ClClO₂, respectively. Similar effects have been observed for bromine/oxygen bonds as well. Another observation from Table 6 is that the central O–N bond length increases from 1.387 Å (6-311G(2d)) to 1.391 Å (6-311G(2df)) to 1.392 Å (6-311+G(3df)). A note must be added here concerning the central O–N bonding in the chlorine nitrates. Examination the Tables 1–6 shows that the central O–N bond in ClOONO₂ is longest and that in O₂ClONO₂ is shortest. In general, with improvements in the basis set, the O–N bond length decreases for species containing two oxygen atoms sandwiched between chlorine and nitrogen (ClOONO₂ and ClOONO₂), while it increases if there are an odd number of oxygen atoms (ClOONO₂, O₂ClONO₂, and ClONO₂). The O–N bonding in ClONO₂ is, however, insensitive to the basis set improvements.

Table 7. B3LYP Harmonic Frequencies (cm⁻¹) and IR Intensities (km/mol)^a for ClOONO₂

mode	approximate description ^b	6-311+G(3df)	TZ2P
$\omega_1(a)$	NO ₂ antisymm str	1844(410)	1819(412)
$\omega_2(a)$	NO ₂ symm str	1362(283)	1353(305)
$\omega_3(a)$	OO str	959(33)	952(38)
$\omega_4(a)$	ON str	793(133)	793(138)
$\omega_5(a)$	NO ₂ wag	716(14)	712(15)
$\omega_6(a)$	ONO bend	658(1)	652(1)
$\omega_7(a)$	OON bend	591(47)	581(55)
$\omega_8(a)$	ClO str	463(11)	457(8)
$\omega_9(a)$	ClOO bend	322(12)	316(10)
$\omega_{10}(a)$	OON wag	304(16)	296(22)
$\omega_{11}(a)$	ClOON torsion	111(0)	111(0)
$\omega_{12}(a)$	OONO torsion	91(0)	90(0)

^a IR absorption intensities in parentheses. ^b Approximate descriptions based upon a total energy distribution analysis.

From Tables 4–6, it can be seen that the central Cl–O single bond distance increases in the order Cl–OOONO₂ < Cl–OONO₂ < O₂Cl–ONO₂, suggesting that the Cl–O central bonds, which are single bonds, are weaker with increasing hypervalent nature of chlorine. As indicated previously, the hypervalent bonding in chlorine is a result of the 3p → 3d promotion of one or two lone-pair chlorine electrons followed by the formation of two or four additional pd hybrid halogen bonds. Hypercoordinate bonding for chlorine is also characterized by a large ionic component relative to normal valent chlorine compounds. A detailed discussion on hypercoordinate bonding of chlorine/oxygen and bromine/oxygen compounds is presented in a recent paper⁴⁹ from our laboratory.

It is interesting to examine the trends in the *ab initio* results for ClONO₂, ClONO₂, and O₂ClONO₂, as all of them contain Cl–O–N skeletons. From Tables S1, 2, and 6, it can be seen that the skeletal Cl–O bond distance increases in the order Cl–ONO₂ < Cl–ONO₂ < O₂Cl–ONO₂. In view of this observation, one might expect the skeletal N–O bond length to decrease in the order of ClO–NO₂ > ClO–NO₂ > O₂ClO–NO₂. That is, one would expect the ClO–NO₂ bond (1.518 Å) to be largest and O₂ClO–NO₂ bond (1.389 Å) to be shortest. But the comparison of Tables S1, 2, and 6 shows that the ClO–NO₂ bond (1.523 Å) is longer than that in the other two species. Another noticeable feature is that there is not a significant change in the NO₂ bond distances in ClONO₂ and ClONO₂, whereas for O₂ClONO₂ the NO₂ bonds are longer. The difference between the two terminal NO₁ and NO₂ bond lengths is 0.012 Å for O₂ClONO₂, while for ClONO₂ and ClONO₂ it is 0.002–0.003 Å. To summarize, the geometrical parameters of the skeletal ClON and NO₂ groups in ClONO₂ and ClONO₂ are similar, while those in O₂ClONO₂ show some differences which can be attributed to the additional terminal ClO bonding in O₂ClONO₂.

It is hoped that the accurate B3LYP equilibrium structures of ClNO₄ and ClNO₅ isomers will aid in the analysis of future experiments and in the complete experimental characterization of the ground electronic states of these species. Also, the rotational constants presented in Tables 1–6 should aid in the experimental characterization of these species using microwave or submillimeter spectroscopic methods.

B. Harmonic Frequencies and IR Intensities. Tables 7–12 report the *ab initio* harmonic vibrational frequencies and IR intensities of isomers of ClNO₄ and ClNO₅ obtained in the

Table 8. B3LYP Harmonic Frequencies (cm⁻¹) and IR Intensities (km/mol)^a for OCIONO₂

mode	approximate description ^b	6-311+G(3df)	TZ2P
$\omega_1(a)$	NO ₂ antisymm str	1832(391)	1768(372)
$\omega_2(a)$	NO ₂ symm str	1356(274)	1333(285)
$\omega_3(a)$	O=Cl str	1006(121)	964(82)
$\omega_4(a)$	ONO ₂ + ONO ₁ bend – O=Cl str	815(152)	816(193)
$\omega_5(a)$	CIONO ₁ – CIONO ₂ torsion	716(11)	743(11)
$\omega_6(a)$	ONO ₁ – ONO ₂ – CION bend + CIO str	686(30)	685(20)
$\omega_7(a)$	ON str	440(13)	440(34)
$\omega_8(a)$	CIO str + ONO ₂ bend	346(6)	371(176)
$\omega_9(a)$	OCIO bend + CIONO ₂ torsion	288(161)	306(43)
$\omega_{10}(a)$	CION bend – OCION torsion	243(1)	230(7)
$\omega_{11}(a)$	CIONO ₁ – CIONO ₂ torsion	126(3)	111(3)
$\omega_{12}(a)$	CIONO ₁ + CIONO ₂ torsion	81(2)	74(2)

^a IR absorption intensities in parentheses. ^b Approximate descriptions based upon a total energy distribution analysis. There is substantial mixing between the Cl–O str, ONO₁ bend, and ONO₂ bend motions.

Table 9. B3LYP Harmonic Frequencies (cm⁻¹) and IR Intensities (km/mol)^a for O₂CINO₂

mode	approximate description ^b	6-311+G(3df)	TZ2P
$\omega_1(a)$	NO ₂ antisymm str	1749(360)	1724(350)
$\omega_2(a)$	NO ₂ symm str	1366(356)	1350(409)
$\omega_3(a)$	CIO ₂ antisymm str	1190(153)	1112(143)
$\omega_4(a)$	CIO ₂ symm str	1011(189)	955(140)
$\omega_5(a)$	NO ₂ bend	776(263)	770(300)
$\omega_6(a)$	NO ₂ rock	559(6)	539(5)
$\omega_7(a)$	CIO ₂ bend	476(14)	449(16)
$\omega_8(a)$	CIO ₂ wag	387(9)	368(8)
$\omega_9(a)$	NCl str	251(6)	248(7)
$\omega_{10}(a)$	ONCl bend	178(2)	174(3)
$\omega_{11}(a)$	OCIO twist	134(0)	132(0)
$\omega_{12}(a)$	NO ₂ twist	41(1)	40(1)

^a IR absorption intensities in parentheses. ^b Approximate descriptions based upon a total energy distribution analysis.

Table 10. B3LYP Harmonic Frequencies (cm⁻¹) and IR Intensities (km/mol)^a for CIOONO₂

mode	approximate description ^b	6-311+G(3df)	TZ2P
$\omega_1(a)$	NO ₂ antisymm str	1845(409)	1815(410)
$\omega_2(a)$	NO ₂ symm str	1363(316)	1351(332)
$\omega_3(a)$	OO str	964(10)	948(10)
$\omega_4(a)$	NO ₂ symm bend	807(171)	810(179)
$\omega_5(a)$	OO str	749(15)	745(16)
$\omega_6(a)$	ON str	729(9)	727(11)
$\omega_7(a)$	CIO str	670(32)	663(36)
$\omega_8(a)$	OOO bend	566(16)	555(17)
$\omega_9(a)$	NO ₂ bend	548(8)	543(14)
$\omega_{10}(a)$	CIOO bend	413(18)	409(20)
$\omega_{11}(a)$	NO ₂ twist	378(20)	381(14)
$\omega_{12}(a)$	OON bend	229(2)	226(2)
$\omega_{13}(a)$	OON torsion	139(0)	140(0)
$\omega_{14}(a)$	OONO torsion	88(0)	86(0)
$\omega_{15}(a)$	CIOOO torsion	64(0)	65(0)

^a IR absorption intensities in parentheses. ^b Approximate descriptions based upon a total energy distribution analysis.

present study together with the limited experimental data available for O₂CINO₂. All the vibrational frequencies are calculated at the B3LYP level of theory using 6-311+G(3df) and TZ2P basis sets. Descriptions of the vibrational modes were obtained from a total energy distribution analysis⁵⁰ of the B3LYP/TZ2P Hessian matrix. It should be noted that the mode

(50) Whitmer, J. C. *J. Mol. Spectrosc.* **1977**, *68*, 326.

Table 11. B3LYP Harmonic Frequencies (cm⁻¹) and IR Intensities (km/mol)^a for OCIOONO₂

mode	approximate description ^b	6-311+G(3df)	TZ2P
$\omega_1(a)$	NO ₂ antisymm str	1833(407)	1813(408)
$\omega_2(a)$	NO ₂ symm str	1356(321)	1348(373)
$\omega_3(a)$	CIO ₃ str	1012(112)	953(99)
$\omega_4(a)$	OO str	966(31)	998(39)
$\omega_5(a)$	ONO bend	790(199)	787(229)
$\omega_6(a)$	ON str	722(18)	710(21)
$\omega_7(a)$	NO ₂ bend	640(40)	633(39)
$\omega_8(a)$	NO ₂ wag	467(2)	456(3)
$\omega_9(a)$	OON bend	445(39)	426(28)
$\omega_{10}(a)$	OCIO bend	377(15)	356(15)
$\omega_{11}(a)$	CIO str	289(2)	264(4)
$\omega_{12}(a)$	CIOO bend	189(1)	167(4)
$\omega_{13}(a)$	CIOON torsion	112(3)	105(2)
$\omega_{14}(a)$	OONO torsion	78(1)	79(1)
$\omega_{15}(a)$	OCIOO torsion	70(3)	57(4)

^a IR absorption intensities in parentheses. ^b Approximate descriptions based upon a total energy distribution analysis.

Table 12. B3LYP Harmonic Frequencies (cm⁻¹) and IR Intensities (km/mol)^a for O₂CIONO₂

mode	approximate description ^b	6-311+G(3df)	TZ2P	expt ^c
$\omega_1(a)$	NO ₂ antisymm str	1682(355)	1650(331)	1658
$\omega_2(a)$	NO ₂ symm str	1317(324)	1302(344)	1275
$\omega_3(a)$	CIO ₂ antisymm str	1263(146)	1191(152)	1250
$\omega_4(a)$	CIO ₂ symm str	1092(146)	1035(140)	1072
$\omega_5(a)$	ON str – ONO ₁ – ONO ₂ bend	885(253)	882(257)	838
$\omega_6(a)$	CIONO ₁ – CIONO ₂ torsion	786(11)	787(12)	
$\omega_7(a)$	ONO ₁ bend	737(34)	728(25)	718
$\omega_8(a)$	ON str + ONO ₂ bend	633(68)	626(48)	613
$\omega_9(a)$	O ₄ CION – O ₃ CION torsion	536(11)	509(13)	
$\omega_{10}(a)$	CIO str – O ₃ CIO – O ₄ CIO + ONO ₂ bend	424(136)	409(121)	
$\omega_{11}(a)$	O ₄ CIO bend + CIO str	289(8)	273(7)	
$\omega_{12}(a)$	O ₃ CIO bend + CIO str	243(34)	229(22)	
$\omega_{13}(a)$	CION–OCIO ₃ bend	145(2)	137(2)	
$\omega_{14}(a)$	O ₃ CION + O ₄ CION + CIONO ₁ + CIONO ₂ torsion	79(1)	75(0.1)	
$\omega_{15}(a)$	O ₃ CION + O ₄ CION – CIONO ₁ – CIONO ₂ torsion	74(0.2)	68(1.1)	

^a IR absorption intensities in parentheses. ^b Approximate descriptions based upon a total energy distribution analysis. ^c Reference 13.

descriptions presented in Tables 7–12 are only approximate, because there is a lot of mixing among the internal coordinate contributions. B3LYP harmonic vibrational frequencies and IR intensities for CIONO₂ are presented as Supporting Information (Table S2). To reduce space, a more detailed discussion of the CIONO₂ harmonic frequencies is also presented as Supporting Information, while only a brief summary is given here.

CIONO₂. Table S2 lists the B3LYP harmonic vibrational frequencies and IR intensities for CIONO₂ together with the experimental fundamental vibrational frequencies.³⁵ Comparison of our *ab initio* harmonic frequencies with the experimental values shows good agreement, especially considering that the anharmonic correction will lower the N–O stretching modes the most. The B3LYP vibrational frequencies of CIONO₂ are in good agreement with the CCSD(T)/TZ2P frequencies reported previously.³¹ As with the equilibrium structure, the good agreement between B3LYP, CCSD(T), and experiment for the harmonic frequencies and, even more importantly, the IR intensities of CIONO₂ leads us to conclude that B3LYP will yield reliable harmonic frequencies and IR intensities for the CINO₄ and CINO₅ isomers as well.

CINO₄ Isomers. The calculated vibrational frequencies for the three isomeric forms of CINO₄ are provided in Tables 7–9. There are no experimental values available for these isomers. As expected, the two highest frequencies of all three isomers are due to terminal NO stretching modes, while the lowest frequencies are due to torsional motions. Terminal Cl–O stretching frequencies are lower than terminal N–O modes due mainly to the larger chlorine mass but also to the fact that terminal NO bonds are generally stronger than terminal ClO bonds. The difference between the central Cl–O or N–O stretching frequencies between the isomers has important implications for the stratospheric chemistry. For example, from Tables 7 and 8, it can be seen that the central N–O stretching frequency (ω_4 ; 793 cm⁻¹) of ClOO–NO₂ is higher than the value for OCIO–NO₂ (ω_7 ; 440 cm⁻¹), suggesting a stronger NO bond. This observation is consistent with the bond lengths. In fact, the central O–N bond length in OCIO–NO₂ is the longest among the seven species considered in this study. Hence, cleavage of the central N–O bond in OCIONO₂ is more favorable than that in ClOONO₂. On the other hand, the Cl–O stretching frequency (ω_8 ; 457 cm⁻¹) for Cl–OONO₂ is lower than that for OCl–ONO₂ (ω_6 ; 685 cm⁻¹), indicating a relatively weak Cl–O bond in ClOONO₂, and indeed, this turns out to be the case; these aspects will be discussed in more detail in the following section. It is also noteworthy that the terminal Cl–O stretching frequencies of O–ClONO₂ (ω_3) and O₂CINO₂ (ω_3 and ω_4) are significantly higher compared to the central Cl–O stretching frequencies of Cl–OONO₂ and OCIO–NO₂ which is due to the presence of double bond character in terminal Cl–O bonds, as discussed in the previous section.

The N–O₂ symmetric and antisymmetric stretches are intense for all three CINO₄ isomers, but OCIONO₂ has an intense band at 371 cm⁻¹ which distinguishes it from the other two isomers, while O₂CINO₂ has an NO₂ bending vibration at 770 cm⁻¹ that should be almost as intense as the N–O₂ antisymmetric stretch. This latter vibration can be used to distinguish O₂CINO₂ from ClOONO₂.

CINO₅ Isomers. For the three isomeric forms of CINO₅, the B3LYP/6-311+G(3df) and B3LYP/TZ2P vibrational frequencies and intensities are presented in Tables 10–12. Similar to the ClONO₂ and the CINO₄ isomers, the two highest frequencies correspond to the terminal N–O stretching modes, while the lowest frequencies are due to torsional motions. As with the geometrical structures, it is interesting to compare the NO₂ stretching frequency values among the CINO₅ isomers. It can be seen from Table 12 that the NO₂ stretching frequencies for O₂CIONO₂ are somewhat lower than those of ClOONO₂ and OCIOONO₂ which are presented in Tables 10 and 11, respectively. This is expected since the NO₂ bond distances in O₂-ClONO₂ are longer than those for the other CINO₅ isomers considered in this study. It is also of note that the NO₂ frequencies for O₂CIONO₂ are somewhat lower than the analogous values for ClONO₂, while those for both ClOONO₂ and OCIOONO₂ are higher than the chlorine nitrate quantities.

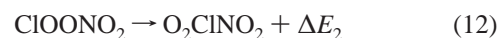
We are not aware of a complete experimental infrared spectra for any CINO₅ isomers, but a partial comparison is possible with the study of Friedl *et al.*¹³ They studied the products of the reaction of OCIO and NO₃ and assigned the infrared spectral features of the product to chloryl nitrate (O₂CIONO₂). Comparison of the B3LYP calculated frequencies and those observed

by Friedl *et al.* (see Table 12) shows excellent agreement between theory and experiment, especially considering that the calculated IR intensities are entirely consistent with the bands actually observed. This is very important since Boyd *et al.*¹⁴ reported that they could not reproduce the results from the Friedl *et al.* study, which raised a doubt regarding the observation of O₂CIONO₂. In summary, our computational results fully support the conclusion by Friedl *et al.* regarding the formation of chloryl nitrate from the association reaction of OCIO and NO₃.

The other noticeably intense bands in these molecules are the terminal ClO stretching frequencies of OCIONO₂, OCIOONO₂, O₂CINO₂, and O₂CIONO₂. The B3LYP/6-311+G(3df) ClO₂ antisymmetric and symmetric stretching frequencies in O₂CIONO₂ (1263, 1092 cm⁻¹) are in excellent agreement with the experimental values (1250, 1072 cm⁻¹). Guha and Francisco²⁸ obtained similar results for the ClO₂ antisymmetric and symmetric stretches in BrClO₂ (1213, 1043 cm⁻¹) calculated at the B3LYP/6-311+G(3df) level. Further, these values are in qualitative agreement with the experimental values⁵¹ for the ClO₂ stretching frequencies of ClClO₂ (1216, 1041 cm⁻¹). The terminal ClO stretch in OCIONO₂ (1006 cm⁻¹) and OCIOONO₂ (1012 cm⁻¹) is comparable to the ClO stretch in BrOCIO (1013 cm⁻¹) calculated²⁸ at the B3LYP/6-311+G(3df) level. Concerning the skeleton NO stretching frequency, no definite trend could be determined, which is probably because of the significant mixing involving this vibration. For the ClON bending frequency, the following trend has been observed, ClONO₂ > OCIONO₂ > O₂CIONO₂. However, all of them are of low intensity. Given the good agreement between theory and experiment for the vibrational frequencies of ClONO₂ and O₂-ClONO₂, the B3LYP frequencies of the other chlorine nitrates reported here, for which no experimental data are available, should be of use in future experimental studies.

The N–O₂ symmetric and antisymmetric stretch frequencies are intense for all three CINO₅ isomers, similar to the situation for the CINO₄ isomers. However, only O₂CIONO₂ has two intense bands above 1000 cm⁻¹ in addition to the N–O₂ symmetric and antisymmetric stretches, and these bands can be used to distinguish O₂CIONO₂ from the other two CINO₅ isomers studied here. Examination of Tables 10 and 11 shows that the OCIOONO₂ isomer can be distinguished from ClOONO₂ by the moderately intense band at 953 cm⁻¹ possessed by the former but not by the latter.

C. Relative Energetics. It is of interest to determine the relative stabilities of the chlorine nitrates. This has been investigated for CINO₄ isomers by computing electronic energies for the following isomerization reactions



The energies are given in Table 13. While the DFT results correspond to geometries optimized at that level of theory, the MP2, CCSD, and CCSD(T) levels of theory using the large ANO2 basis set are evaluated from single-point energies for the B3LYP/TZ2P equilibrium geometries. For convenience, the energies, in kcal/mol, that OCIONO₂ and O₂CINO₂ are above ClOONO₂ have been denoted as ΔE_1 and ΔE_2 , respectively. From Table 13, it can be seen that the lowest energy is possessed by ClOONO₂. The next lowest energy structure is that of the

Table 13. Relative Energies^a of the ClOONO₂, OCIONO₂, and O₂ClONO₂ Isomers

theory	ClOONO ₂	ΔE ₁	ΔE ₂
B3LYP/6-311G(2d)	1.692 36	21.7	29.5
B3LYP/6-311G(2df)	1.706 33	18.6	23.8
B3LYP/6-311+G(3df)	1.723 60	12.0	14.8
B3LYP/TZ2P	1.731 64	19.3	28.9
MP2/ANO2	0.612 46	9.6	6.3
CCSD/ANO2	0.599 93	16.3	30.2
CCSD(T)/ANO2	0.677 40	14.8	21.1
ΔZPVE ^b		-0.4	-0.4

^a The total energy of ClOONO₂, in Hartree units, is given as $-(E + 814)$, and the energies that OCIONO₂ and O₂ClONO₂ are above ClOONO₂ are given in kcal/mol as ΔE₁ and ΔE₂, respectively. ^b Zero-point vibrational energies derived from the B3LYP/TZ2P harmonic frequencies.

Table 14. Relative Energies^a of the ClOOONO₂, OCIOONO₂, and O₂ClONO₂ Isomers

theory	ClOOONO ₂	ΔE ₃	ΔE ₄
B3LYP/6-311G(2d)	1.855 82	19.8	14.3
B3LYP/6-311G(2df)	1.872 15	18.0	7.6
B3LYP/6-311+G(3df)	1.892 26	14.3	-1.1
B3LYP/TZ2P	1.902 77	17.9	15.1
MP2/ANO2	0.656 76	11.3	-11.9
CCSD/ANO2	0.644 19	22.7	8.4
CCSD(T)/ANO2	0.733 74	16.7	4.1
ΔZPVE ^b		-0.4	0.6

^a The total energy of ClOOONO₂, in Hartree units, is given as $-(E + 889)$, and the energies that OCIOONO₂ and O₂ClONO₂ are above ClOOONO₂ are given in kcal/mol as ΔE₃ and ΔE₄, respectively. ^b Zero-point vibrational energies derived from the B3LYP/TZ2P harmonic frequencies.

OCIONO₂ isomer, and the highest energy structure is that of the O₂ClONO₂ isomer. The results exhibit a noticeable dependence on the treatment of electron correlation and basis set. At the B3LYP level, the relative energies decrease with basis set improvement. On the basis of experience,^{29–35} we consider the CCSD(T)/ANO₂ energy differences as our best estimate. Including the effects of zero-point energies (derived using the B3LYP/TZ2P harmonic frequencies) reduces ΔE₁ by 0.4 kcal/mol, giving a final estimate of 14.4 kcal/mol at the CCSD(T)/ANO₂ level of theory. Similarly, the O₂ClONO₂ isomer is predicted to be 20.7 kcal/mol higher in energy at the CCSD(T)/ANO₂ level of theory relative to ClOONO₂ after accounting for zero-point vibrational energies.

Relative energies for the ClNO₅ isomers are presented in Table 14. The energy differences ΔE₃ and ΔE₄ are defined according to eqs 13 and 14.



The ΔE values again demonstrate that the MP2 method is not capable of determining this energy difference accurately. Relative energy calculations for the three isomers of ClNO₅ show that the structure possessing the lowest energy is that of the ClOOONO₂ isomer. Taking CCSD(T)/ANO₂ energy differences as our best computed values and correcting these for zero-point vibrational energy differences (see Table 14) yields 16.3 and 4.7 as our best estimates for ΔE₃ and ΔE₄, respectively (note that these are for 0 K). Thus, our best estimate is that ClOOONO₂ is lower in energy than O₂ClONO₂ and OCIOONO₂. However, the uncertainty allows for the possibility that O₂-

ClONO₂ may in fact be the lowest energy isomer of ClNO₅. Under atmospheric or experimental conditions, it is currently not possible to say definitively whether ClOOONO₂ or O₂-ClONO₂ is lower in energy. The results of this study, however, allow us to say with certainty that ClOOONO₂ and O₂ClONO₂ are very close in energy. The ultimate importance of ClOOONO₂ and O₂ClONO₂ in atmospheric chemistry must therefore be determined by kinetic stability, formation rates, and the barrier separating ClOOONO₂ and O₂ClONO₂ interconversion. To the extent possible, formation rates for these two compounds will be addressed in section E, Atmospheric Implications, and their importance to Earth's atmospheric chemistry is discussed in relation to their formation rates.

D. Bonding and Heats of Formation. Additional insight into the difference of the bonding in the chlorine nitrates may be gained by comparing the Mulliken populations. The B3LYP/TZ2P values are presented in Table 15. For convenience, the three species, ClONO₂, OCIONO₂, and O₂ClONO₂, are grouped together, all of which contain a ClON skeleton bonding. For the three XONO₂ (X = Cl, ClO, ClO₂) molecules, the N atom has the same largest positive partial charge. The negative partial charges for the central oxygen and terminal O₁ atoms are fairly consistent for the three molecules, but the partial charge on the O₂ atom, which is in the trans position relative to the skeletal ClON structure, increases noticeably for the O₂ClONO₂ molecule. The chlorine atom exhibits a positive partial charge for all three equilibrium structures and, as expected, the magnitude increases with the coordination number. That is, the partial positive charge for the Cl atom increases in the order ClONO₂ < OCIONO₂ < O₂ClONO₂. These observations are entirely consistent with the Mulliken populations found previously³⁰ for the analogous bromine compounds. In general, like many other halogen compounds where other electronegative elements are present (for example, see ref 49 and the discussion therein), the Mulliken populations indicate that there is a substantial ionic component to the bonding in XONO₂ molecules. Inspection of the chlorine atom partial charges presented in Table 15 shows that the degree of ionic bonding increases with the coordination number of chlorine. The Mulliken populations also provide an explanation for why the O₂ClONO₂ isomer is much less stable than OCIONO₂ and ClOONO₂. That is, for the O₂ClONO₂ species, the Cl atom, with the largest positive charge, is bonded to the positively charged N atom, while, for OCIONO₂ and ClOONO₂, a negatively charged oxygen atom is between the positively charged Cl and N atoms. It is apparent that the ionic contribution to the bonding is a deciding factor on the relative stability of the isomers.

To assess the possible importance of these higher oxides of chlorine nitrate to atmospheric chemistry, it is important to know their stability with respect to possible dissociation pathways. The first step in this assessment is to determine their heat of formation (ΔH_f^o). In the present study, we utilize *ab initio* molecular orbital calculations and isodesmic reactions to calculate ΔH_f^o for the halogen nitrates. The method of isodesmic reactions relies upon the similarity in bonding environment of the reactants and products that leads to cancellation of any deficiencies in the *ab initio* molecular orbital calculation. In this approach, the ΔH_f^o of a particular species can be evaluated from the calculated heat of reaction ΔH_{rxn}^o and the known ΔH_f^o of the other species involved in the reaction. Since reliable

Table 15. Atomic Charge Distributions Based on Mulliken Population Analyses for XONO₂ at the B3LYP/TZ2P Level of Theory^a

	ClONO ₂	OClONO ₂	O ₂ ClONO ₂		ClONO ₂	OClONO ₂	ClOOONO ₂		O ₂ ClONO ₂	
Cl	+0.16	+0.67	+1.12	Cl	+0.08	+0.58	Cl	+0.11	O ₃	-0.44
O	-0.21	-0.25	-0.28	O ^c	-0.10	-0.15	O ^c	-0.14	O ₄	-0.45
N	+0.55	+0.55	+0.55	O	-0.06	-0.05	O	+0.03	Cl	+0.94
O ₁	-0.25	-0.24	-0.26	N	+0.54	+0.54	O	-0.08	N	+0.38
O ₂	-0.25	-0.25	-0.33	O ₁	-0.23	-0.24	N	+0.55	O ₁	-0.21
O ₃		-0.47 ^b	-0.40	O ₂	-0.24	-0.23	O ₁	-0.23	O ₂	-0.23
O ₄			-0.39	O ₃		-0.44 ^b	O ₂	-0.24		

^a See Figures 1–3 for labeling of atoms. ^b This is the terminal oxygen bonded to the Cl atom. ^c This is the central oxygen bonded to the Cl atom.

Table 16. Energies (kcal/mol) for the Isodesmic Reactions 15–22 using B3LYP/TZ2P Geometries^a

	ΔE_5	ΔE_6	ΔE_7	ΔE_8	ΔE_9	ΔE_{10}	ΔE_{11}	ΔE_{12}
B3LYP/TZ2P	2.5	-3.7	-10.3	-28.9	1.4	-37.2	-11.5	-46.0
HF/ANO2	2.9	3.8	-0.5	-17.8	5.1	-12.7	-11.1	-33.4
MP2/ANO2	0.2	-3.8	-10.0	-35.2	0.8	-46.7	-13.3	-55.4
CCSD/ANO2	1.6	-1.2	-7.0	-27.3	2.3	-29.1	-12.2	-42.6
CCSD(T)/ANO2	1.3	-3.0	-9.5	-30.6	1.4	-37.2	-12.7	-46.7
$\Delta ZPVE^b$	-0.0	-0.5	-1.4	-0.3	-0.5	-1.6	-1.3	-0.7
ΔVT^c	0.1	0.2	0.5	0.5	0.3	1.1	0.5	0.9

^a Zero-point vibrational energies not included; see text for energy differences where these are included. ^b Zero-point vibrational energies determined using B3LYP/TZ2P harmonic frequencies. ^c Energy changes due to thermal population of vibrational energy levels at 298.15 K.

experimental thermodynamic data for some of the chlorine compounds are not available in the literature, we used calculated ΔH_f° values wherever there are no experimental data available.

The heat of formation of ClONO₂ has been examined in our earlier study³¹ and calculated to be 7.4 kcal/mol at 298 K, in good agreement with the experimental value 6.3 ± 0.2 kcal/mol. We have used the following isodesmic reactions to determine the heat of formation of ClOOONO₂ (reactions 15–17), OClONO₂ (18 and 19), O₂ClONO₂ (20), ClOOONO₂ (21), and O₂ClONO₂ (22).



Single-point HF, MP2, CCSD, and CCSD(T) energies have been evaluated for all of the species involved in reactions 15–22 using the ANO2 basis set. In all cases, B3LYP/TZ2P geometries have been used. Table 16 contains a summary of the ΔE values obtained from reactions 15–22, together with contributions due to zero-point vibrational energies ($\Delta ZPVE$) and thermal population of vibrational energy levels (ΔVT). All of the species involved in reactions 15–22 have three rotational degrees of freedom except for HCl which has two rotational degrees of freedom. Therefore, in reactions 18, 20, and 22, the ΔVT values are reported after accounting for the difference in rotational energies of reactants and products by subtracting $1/2RT$ from the ΔVT , where R is the molar gas constant. A quick examination of the results in Table 16 shows that the ΔE values

calculated at the B3LYP/TZ2P level of theory are in good agreement with those determined at the CCSD(T)/ANO2 level of theory. This is interesting, because although B3LYP geometries and vibrational frequencies have been found to be reasonably reliable, B3LYP energetics are not nearly as reliable as demonstrated by the results in Tables 13 and 14, as well as previous studies (for example, see ref 27). It would seem that the use of isodesmic reactions has, to a large extent, canceled the inherent error in the B3LYP energetic results. The reaction energies ΔE_5 and ΔE_{11} exhibit little effect due to the level of theory, indicating that the reactions 15 and 21 are very good isodesmic reactions. Thus, based on experience,^{27–31} the CCSD(T)/ANO2 ΔE_5 and ΔE_{11} reaction energies are expected to be accurate to better than ± 0.5 kcal/mol, while, for the other reaction energies included in Table 16, the CCSD(T)/ANO2 result is probably accurate to within ± 1.0 kcal/mol. Hence, even when using isodesmic reactions, for compounds composed of several electronegative atoms bonded together, it is best to use the highest level of theory available.

Taking the CCSD(T)/ANO2 reaction energies as our best estimate and correcting these for the effects of zero-point vibrational energy and thermal population of vibrational energy levels (298.15 K; see Table 16) yields 1.3, -3.0, -9.5, -30.6, 1.4, -37.2, -12.7, and -46.7 for ΔE_5 through ΔE_{12} , respectively. Combining these *ab initio* reaction energies with experimental heats of formation for ClONO₂ from ref 52, BrONO₂ and HOBr from ref 53, HOCl and HCl from ref 54 and calculated heats of formation for HOClO and HClO₂ from ref 55 and HClO from ref 56 gives 20.0, 20.9, and 21.2 kcal/mol for $\Delta H_{f,298}^\circ(\text{ClOOONO}_2)$ from reactions 15–17, 33.3 and 33.9 kcal/mol for $\Delta H_{f,298}^\circ(\text{OClONO}_2)$ from reactions 18 and 19, and 38.0 kcal/mol for $\Delta H_{f,298}^\circ(\text{O}_2\text{ClONO}_2)$ from reaction 20. Because reactions 15 and 19 appear to be the better isodesmic reactions (see Table 16), we take 20.0 and 33.9 kcal/mol as our best estimates for $\Delta H_{f,298}^\circ(\text{ClOOONO}_2)$ and $\Delta H_{f,298}^\circ(\text{OClONO}_2)$, respectively, although it should be noted that the excellent agreement obtained using the different isodesmic reactions for $\Delta H_{f,298}^\circ(\text{ClOOONO}_2)$ and $\Delta H_{f,298}^\circ(\text{OClONO}_2)$ indicates the internal consistency of the data and provides confidence in the heats of formation for those compounds where only one isodesmic reaction could be used. It is interesting to compare literature estimates⁵⁷ for the heats of formation for ClOOONO₂

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(56) Lee, T. J. *J. Phys. Chem.* **1994**, *98*, 3697; the CCSD(T)/ANO4 energy difference between HOCl and HClO has been added to the $\Delta H_{f,298}^\circ(\text{HOCl})$ to obtain $\Delta H_{f,298}^\circ(\text{HClO})$.

(57) Grell, M. A.; Colussi, A. *J. Phys. Chem.* **1996**, *100*, 10150.

and OCIONO₂ to the present calculations. Grela and Colussi⁵⁷ reported the heat of formation based on group additivity methods. For ClOONO₂ and OCIONO₂, they estimated the heats of formation to be 19.0 and 26.5 kcal/mol, respectively. While the ClOONO₂ bond additivity value is close to our calculated heat of formation, their estimated value for OCIONO₂ is about 7.0 kcal/mol smaller than the value obtained here.

Using a similar procedure, we obtained the heats of formation for the ClNO₅ isomers. Combining the *ab initio* reaction energies with the experimental or calculated heats of formation as noted above, we obtain 32.7 kcal/mol for $\Delta H_{f,298}^{\circ}(\text{ClOONO}_2)$ from reaction 21 and 32.6 kcal/mol for $\Delta H_{f,298}^{\circ}(\text{O}_2\text{ClONO}_2)$ from reaction 22. Note that Friedl *et al.*¹³ estimated a value of 22.0 ± 3.0 kcal/mol which is about 10.0 kcal/mol smaller than our predicted value for O₂ClONO₂. Note also, that, contrary to the direct calculation of isomerization energies reported in Table 14, the use of isodesmic reactions has actually found O₂ClONO₂ to be the most stable isomer, albeit by only 0.1 kcal/mol. We note that the calculation of relative energies using the heats of formation obtained from isodesmic reactions should be more reliable, provided the experimental/calculated heats of formation for the “known” molecules are reliable.

The heat of formation for OCIONO₂ can be obtained by adding our best estimate for ΔE_3 (from Table 14) to the calculated heat of formation for ClOONO₂. Performing this step, we obtain 49.0 kcal/mol for $\Delta H_{f,298}^{\circ}(\text{OCIONO}_2)$.

E. Atmospheric Implications. The thermal stability of OCIONO₂, ClOONO₂, and O₂ClNO₂ can be determined from their heats of formation given above. When ClOONO₂ is considered first, the most likely thermal dissociation channels are



Combining the $\Delta H_{f,298}^{\circ}(\text{ClOONO}_2)$ value determined in this work with experimental heats of formation for Cl, ClO, ClOO, NO₂, and ONO₂ from ref 54 yields ClOO–NO₂ and ClO–ONO₂ bond energies of 11.3 and 21.3 kcal/mol, respectively. We are not aware of an experimental heat of formation for OONO₂; however, Grela and Colussi⁵⁷ have reported it to be 18.4 kcal/mol based on the bond additivity method which indicates that the Cl–O bond in ClOONO₂ is relatively stable.

For OCIONO₂, the most likely thermal dissociation channels are

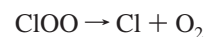
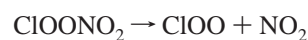
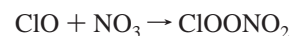
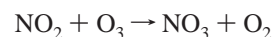
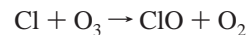


and, for O₂ClNO₂,

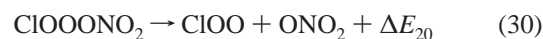


Using the information detailed above, ΔE_{16} , ΔE_{17} , and ΔE_{18} are computed to be –2.8, 7.4, and –6.9 kcal/mol (298 K), respectively. The ΔE_{16} and ΔE_{18} values clearly indicate that the OCIONO₂ and O₂ClNO₂ are very weakly bound isomers of ClNO₄ and may be only metastable. This implies that ClOO formation from the reaction of ClO with NO₃ should dominate

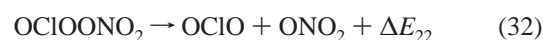
over OCIO formation because the formation of ClOONO₂ from ClO + NO₃ (reaction 5) is much more exothermic than the formation of OCIONO₂ (reaction 7). Note that this is also consistent with the expectation that the open-shell electron in ClO should reside mainly on the oxygen atom and not the chlorine atom. These observations are consistent with the experimental investigation of the reaction between ClO and NO₃ which suggested that the formation of OCIO and NO₂ would be a minor product channel.^{16,17} Based on the fact that concentrations of Cl and NO₂ are non-negligible in the stratosphere and that ClOO formation is the most likely product from the reaction of ClO and NO₃, it can be inferred that the following cycle plays some role in stratospheric chemistry:



Similar to the ClNO₄ isomers, the thermal stability of ClOONO₂, OCIONO₂, and O₂ClONO₂ can be determined from their heats of formation. For ClOONO₂, the most likely thermal dissociation channels are

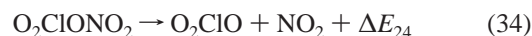


For OCIONO₂, the likely dissociation channels are



With the use of heats of formation for products from ref 54 and the presently calculated $\Delta H_{f,298}^{\circ}$ for ClOONO₂ and OCIONO₂, the ΔE_{19} , ΔE_{20} , and ΔE_{22} quantities are computed to be 21.6, 7.7, and –8.8 kcal/mol, respectively. Using the heat of formation of OONO₂ from ref 57 yields ΔE_{21} and ΔE_{23} values of 10.0 and –6.3 kcal/mol, respectively. From these values, we can conclude that ClOONO₂ is thermally stable but that the OCIONO₂ isomer is only metastable.

For O₂ClONO₂, it is of interest to examine the O₂ClO–NO₂ and O₂Cl–ONO₂ bond energies since they are the two weakest bonds and thus are the most susceptible to thermal dissociation:

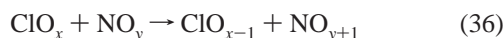


Using the experimental heats of formation of products from ref 54 together with the computed $\Delta H_{f,298}^{\circ}$ value for O₂ClONO₂, we obtain 21.7 and 7.6 kcal/mol for ΔE_{24} and ΔE_{25} , respectively. Thus, it is evident that O₂ClONO₂ has a thermal stability on par with that for ClOONO₂, again suggesting that these two isomers are very close in energy.

Table 17. Equilibrium Constants for ClO_x + NO_y Reactions

temperature (K)	reaction 37	reaction 38	reaction 39
200	4.1×10^{-16}	2.0×10^{-20}	2.8×10^{-20}
210	9.9×10^{-17}	7.5×10^{-21}	1.1×10^{-20}
220	2.7×10^{-17}	3.0×10^{-21}	4.6×10^{-21}
230	8.2×10^{-18}	1.3×10^{-21}	2.1×10^{-21}
240	2.8×10^{-18}	6.3×10^{-22}	1.0×10^{-21}
250	1.0×10^{-18}	3.2×10^{-22}	5.2×10^{-22}
260	4.1×10^{-19}	1.7×10^{-22}	2.8×10^{-22}
270	1.7×10^{-19}	9.3×10^{-23}	1.6×10^{-22}
280	7.9×10^{-20}	5.4×10^{-23}	9.5×10^{-23}
290	3.8×10^{-20}	3.3×10^{-23}	5.9×10^{-23}
300	1.9×10^{-20}	2.0×10^{-23}	3.7×10^{-23}
310	1.0×10^{-20}	1.3×10^{-23}	2.4×10^{-23}
320	5.6×10^{-21}	8.7×10^{-24}	1.7×10^{-23}

Finally, the equilibrium constant for the following reactions is calculated to ascertain whether these species are important in the atmosphere as reservoir species or as intermediate complexes in the chemically activated reactions,



Based on the thermal stabilities determined above, the reactions considered are



The equilibrium constant for these reactions is estimated from partition functions using statistical thermodynamics.⁵⁸ The translational, vibrational, rotational, and electronic partition functions are calculated from the *ab initio* structural, vibrational, and binding energy data given. The equilibrium constant, which is in units of cm³ molecule⁻¹, is found by dividing the total partition function of the product (the complex) by the total partition function of the reactants. The equation for this calculation, as given in ref 58, is

$$K_c(T) = \rho\text{ClO}_x - \text{NO}_y / \rho\text{ClO}_x \rho\text{NO}_y \quad (40)$$

where $K_c(T)$ is the temperature-dependent equilibrium constant in terms of concentration and $\rho\text{ClO}_x - \text{NO}_y$, ρClO_x , and ρNO_y are the total partition functions of the complex and reactants. The equilibrium constants for reactions 37–39 are calculated over the temperature range from 200 to 320 K and are presented in Table 17. For reaction 37, at the higher temperature, the equilibrium constant is estimated to be on the order of 10⁻²¹, while, at the lower temperatures, it increases by 5 orders of magnitude. Consequently, lower temperatures will favor the formation of ClOONO₂. It is interesting to note that, at 210 K, a temperature region characteristic of the lower stratosphere, the equilibrium constant for reaction 37 is $\sim 10^{-16}$. This is quite close to the equilibrium constant for the ClO dimer (ClOOCi),^{59,60} which is 7×10^{-15} , suggesting that ClOONO₂ could be a possible new reservoir species. However, its abundance may

be small because the essential reactant for its formation, ClOO, is of low concentration in the lower stratosphere.⁶¹

For reaction 38, the equilibrium constant is significantly smaller relative to reaction 37. At the higher temperatures, the equilibrium constant is on the order of 10⁻²⁴. The equilibrium constant only increases 3 orders of magnitude over the lower temperature range. Note that, over the lower temperature range, the equilibrium constant for reaction 38 is 4 orders of magnitude smaller than that for reaction 37. Coupling this with the smaller abundance of ClOO, we suggest that the ClOOONO₂ species is only likely to be an intermediate complex in the ClOO + NO₃ reaction.

For reaction 39, the equilibrium constant at higher temperatures is on the order of 10⁻²³ and at lower temperature ranges to 10⁻²⁰. Friedl *et al.*¹³ derived an expression for the equilibrium constant for the OCIO + NO₃ reaction as

$$K(T) = 1 \times 10^{-28} \exp(9300/T) \quad (41)$$

Over the temperature range from 200 to 300 K, the equilibrium constant varies over 10 orders of magnitude. Our calculations suggest that the equilibrium constant varies only over 3 orders of magnitude (see Table 17). At 220 K, where the laboratory experiments of Friedl *et al.* were performed, the equilibrium constant they calculate is 2.3×10^{-10} . Our estimate of the equilibrium constant at this temperature is 4.6×10^{-21} . This is more than a 10 orders of magnitude difference. The source of discrepancy in these results lies in the difference between the binding energy used by Friedl *et al.* and that calculated in this study. Friedl *et al.* estimated the binding energy of O₂ClONO₂ to be 18 ± 3 kcal/mol, while our calculation estimates the binding energy to be 7.6 kcal/mol. There is a 10.4 kcal/mol difference, and this large difference is reflected in the equilibrium constants. We do not find the thermal stability of O₂ClONO₂ to approach that of ClOOCi (ClO dimer), but rather we find it to be more similar to ClOO. At about 20 km, the abundances of NO₂ and OCIO are 1×10^9 and 1×10^7 molecules cm⁻³, respectively. If we use the equilibrium constant of Friedl *et al.*, the abundance of O₂ClONO₂ is roughly 2×10^6 . This is consistent with their number density estimate of O₂ClONO₂. If we use the present calculated equilibrium constant, the abundance of O₂ClONO₂ is negligible. We can only conclude that there will not be a significant source of O₂-ClONO₂ from the OCIO + NO₃ reaction in the atmosphere. Other sources of O₂ClONO₂ are possible, for example, from the ClO₃ + NO₂ reaction. However, abundances of ClO₃ have not been measured in the atmosphere. Although the present calculations, based on equilibrium constants and atmospheric abundances, suggest that O₂ClONO₂ may have no atmospheric chemical relevance, our earlier calculations on the thermodynamic stability and vibrational spectrum of O₂ClONO₂ indicate that under laboratory conditions the formation of O₂ClONO₂ cannot be ignored.

Conclusions

The equilibrium structures, dipole moments, and vibrational spectra of ClNO_x ($x = 4$ and 5) molecules have been studied at the B3LYP level of theory using four large basis sets. In general, the B3LYP results showed little dependence on the basis set

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with bond distances typically varying by less than 0.050 Å and bond angles by only tenths of a degree. The 6-311G(2d) basis set usually gave the longest Cl–O bond lengths, and the 6-311+G(3df) basis set gave the shortest bond lengths. Good agreement was found with a previous *ab initio* coupled-cluster study and experiment for ClONO₂. These observations confirm that B3LYP can predict very good geometries for molecules containing chlorine, oxygen, and nitrogen atoms. Furthermore, very good agreement was found between the present study and a previous experimental¹³ study concerning the vibrational frequencies of O₂ClONO₂, which strongly supports their analysis, contrary to a later experimental study.¹⁴ Based on the good agreement between the available experimental data and the present theoretical results, it is expected that the *ab initio* geometries and vibrational spectra for the other ClNO₄ and ClNO₅ species will aid in their experimental characterization.

Using isodesmic reactions, heats of formation have been evaluated using CCSD(T) in conjunction with a large ANO basis set. $\Delta H_{f,298}^{\circ}$ values are determined to be 20.0, 33.9, 38.0, 32.7, 49.0, and 32.6 kcal/mol for ClOONO₂, OClONO₂, O₂ClNO₂, ClOOONO₂, OClOOONO₂, and O₂ClONO₂, respectively.

Friedl *et al.*¹³ have shown that O₂ClONO₂ is a product of the reaction between OClO and NO₃, and the agreement between our computed and the experimental vibrational frequencies

conclusively demonstrates this point. The results of this study suggest that both ClOOONO₂ and O₂ClONO₂ are thermally stable enough to be possible minor stratospheric chlorine reservoir species, as suggested previously,¹³ but their importance in stratospheric chemistry may be minimal since the abundance of the reactants in the known formation channels is too small to allow for significant concentrations in the atmosphere. We note that, from consideration of the photostability of similar molecules,⁶² O₂ClONO₂ is likely to be much more photostable than ClOOONO₂.

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Supporting Information Available: A more detailed discussion of the B3LYP equilibrium geometry of ClONO₂, B3LYP optimized structure and structural parameters for ClONO₂, and B3LYP harmonic frequencies for ClONO₂ with the complete set of experimental frequencies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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