THE JOURNAL OF
PHYSICAL
CHEMISTRY A
LETTERS

2008, *112,* 9623–9627
Published on Web 09/09/2008

$ClClO_2$ Is the Most Stable Isomer of Cl_2O_2. Accurate Coupled Cluster Energetics and Electronic Spectra of Cl_2O_2 Isomers

Myrna H. Matus, Minh T. Nguyen, and David A. Dixon*

Department of Chemistry, The University of Alabama, Shelby Hall, Box 870336, Tuscaloosa, Alabama 35487-0336

Kirk A. Peterson*

Department of Chemistry, Washington State University, Pullman, Washington 99164-4630

Joseph S. Francisco

Department of Chemistry and Department of Earth & Atmospheric Sciences, Purdue University, West Lafayette, Indiana 47907-2084

Received: July 14, 2008; Revised Manuscript Received: August 26, 2008

High level ab initio electronic structure calculations at the coupled cluster level with a correction for triples (CCSD(T)) extrapolated to the complete basis set limit have been made for the thermodynamics of the Cl_2O_2 isomers: $ClClO_2$, ClOOCl, and ClOClO. The $ClClO_2$ isomer is predicted to be the most stable isomer and is more stable than ClOOCl by 3.1 kcal/mol at 298 K. The ClOClO isomer is less stable than ClOOCl by 8.3 kcal/mol at 298 K. The weakest bond in $ClClO_2$ is the Cl−Cl bond with a bond dissociation energy (BDE) of 24.4 kcal/mol, and the smallest BDE in ClOOCl is the O−O bond with a value of 18.0 kcal/mol. The smallest BDE in ClOClO is for the central O−Cl bond with a BDE of 9.7 kcal/mol. Electronic transitions were calculated with the equations of motion EOM-CCSD method. The calculations clearly demonstrate that singlet states of $ClClO_2$ absorb to longer wavelengths in the visible than do the singlet states of ClOOCl as does ClOClO.

Since Molina and Rowland's paper[1] on the role of chlorine atoms in the destruction of ozone in the stratosphere, there has been substantial interest in the nature of the chlorine oxides,[2] notably ClOOCl which is formed by the dimerization of two ClO molecules.[3,4] This molecule photodissociates to form ClOO and Cl, and the ClOO molecule rapidly decomposes to form Cl + O_2. The Cl atoms then participate in the usual Cl catalyzed destruction of O_3 via reaction (1).

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (1)$$

There is renewed interest in the ultraviolet absorption spectrum of ClOOCl due to a recent study by Pope et al.[5] that showed that the photoabsorption cross sections of ClOOCl at wavelengths longer than 300 nm are significantly lower than all previous measurements or estimates.[6−12] This is critical as the absorption at wavelengths longer than 300 nm is the most important for predicting the photolysis rate of ClOOCl as ozone absorbs most of the shorter wavelengths in this region of the atmosphere. The latest experimental work used very carefully purified ClOOCl to minimize the contributions of impurities that could increase the longer wavelength cross-section. Because photolysis of ClOOCl is the rate limiting step in the loss of polar ozone, it is critical to understand different potential absorbers. There is substantial concern in the atmospheric modeling community as to what the correct chemistry is to account for ozone depletion in the stratosphere.[2,13]

Computational chemistry approaches have reached the point where the combination of electronic structure methods (coupled cluster[14] or multireference configuration interaction[15]), correlation-consistent basis sets that extrapolate to the complete basis set limit,[16] and high performance computers allow us to predict the structures and energies of medium size molecules to chemical accuracy.[17] This has already been done for the XO diatomics (X is a halogen).[18] Of interest to the current problem with the photoabsorption cross section of ClOOCl is the fact that there are three relevant isomers with the formula Cl_2O_2: ClOOCl, $ClClO_2$, and ClOClO.[19] Müller and Willner reported the first synthesis of $ClClO_2$ in a matrix as well as its spectroscopic characterization in 1992.[20] McKeachie et al.[21] observed the formation of $ClClO_2$ from reactions of ClO on/in water ice surfaces and Pursell et al.[22] observed the formation of $ClClO_2$ in studies of the photolysis of OClO in polycrystalline ice. Lee et al.[23] used coupled cluster theory with a perturbative triples correction (CCSD(T)) with atomic natural orbital basis sets to predict that the $ClClO_2$ isomer is only 0.9 ± 2.0 kcal/mol above the energy of ClOOCl and, in fact, could lie lower in energy. They also predicted the isomer ClOClO to be 10.1 ± 4.0 kcal/mol higher in energy. Since Lee et al.'s work, there have been a number of experimental advances including the experimental determination[24] of the structure of $ClClO_2$ as well

---

* To whom correspondence should be addressed.

10.1021/jp806220r CCC: \$40.75

as more theoretical studies[25] which included modified G2 calculations[26] with density functional theory (B3LYP exchange-correlation functional[27]) geometries of the PES for interconversion of the Cl_2O_2 isomers. The latter results predict a barrier of 19 kcal/mol to convert ClOClO to $ClClO_2$ and a barrier of 12 kcal/mol to convert ClOClO to ClOOCl. Kaledin and Morokuma performed direct dynamics complete active space self-consistent field (CASSCF) calculations on the photodissociation of ClOOCl and showed that translationally hot Cl atoms and rotationally excited O_2 are expected to be the most important photodissociation products.[28] G2 calculations of the relative energies of the isomers predict that ClOOCl is the most stable isomer with the $ClClO_2$ isomer 6.8 kcal/mol higher in energy and the ClOClO isomer even higher in energy (11.9 kcal/mol) at 298 K.[29]

We have used high level molecular orbital theory following the methods we developed for accurate thermochemical predictions[17] to predict the structures, vibrational frequencies, and heats of formation of the Cl_2O_2 isomers and additional compounds with the stoichiometry Cl_xO_y for x, $y = 1, 2$. All thermochemical calculations were done with the R/UCCSD(T) method[30] with correlation consistent basis sets[31] including tight d functions up through aug-cc-pV(n+d)Z with $n = 5$. Geometries were optimized up through $n = \mathrm{T}$ and in some cases for $n = \mathrm{Q}$. The frequencies were all calculated at $n = \mathrm{T}$ and used to calculate the zero point energy (ΔE_{ZPE}) except for ClClO ($^3A''$) where the MP2/aug-cc-pV(T+d)Z frequencies were used. The valence electronic energies were extrapolated to the complete basis set limit (ΔE_{elec}(CBS)) using an $l_{\max}{}^3$ expansion for $n = \mathrm{Q}$ and 5.[32,33] The scalar relativistic corrections (ΔE_{SR}) were carried out at the CCSD(T)/Douglas−Kroll−Hess level[34] with the cc-pVTZ-DK basis sets. The core valence corrections (ΔE_{CV}) were done at the CCSD(T)/cc-pwCVTZ level[35] and, for the Cl_2O_2 isomers, the core valence corrections were also obtained with the cc-pwCVQZ basis set. Atomic spin orbit corrections (ΔE_{SO}) were taken from the tables of Moore[36] and a molecular spin orbit correction of 0.45 kcal/mol was used for ClO.[44] The total atomization energy is calculated from eq 2 and the various terms are given in the Supporting Information

$$\sum D_0 = \Delta E_{\mathrm{elec}}(\mathrm{CBS}) - \Delta E_{\mathrm{ZPE}} + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{SR}} + \Delta E_{\mathrm{SO}} \quad (2)$$

Heats of formation were calculated by combining our computed ΣD_0 values with the known enthalpies of formation at 0 K for the elements ($\Delta H_f^0(\mathrm{Cl}) = 28.59 \pm 0.001$ kcal/mol and $\Delta H_f^0(\mathrm{O}) = 58.98 \pm 0.02$ kcal/mol). We obtain enthalpies of formation at 298 K by following the procedures outlined by Curtiss et al.[37] The ab initio calculations of this work utilized predominately the MOLPRO program[38] except for the triplet excitation energy calculations which employed the DALTON package.[39]

The molecular geometries are given in the Supporting Information. The agreement of the calculated structure with the experimental geometry[24] for $ClClO_2$ is excellent, within 0.5° and a few thousandths of an angstrom. For ClOOCl, there is a larger error in the calculated geometry as compared to experiment[40] with the O−O distance predicted too short by 0.02 Å and the Cl−O distance too long by 0.01 Å even with the aug-cc-pV(Q+d)Z basis set. This is consistent with calculations on FOOF.[41] The predicted equilibrium structures with the aug-cc-pV(T+d)Z basis set are within 0.01 Å of the experimental geometries for OClO,[42] ClOCl,[7,43] ClO,[44] and Cl_2,[44] a difference expected on the basis of other calculations and with our results for $ClClO_2$.

The calculated vibrational frequencies (Supporting Information) serve as an additional test of the accuracy of the present results. For $ClClO_2$, the calculated CCSD(T)/aug-cc-pV(T+d)Z harmonic frequencies are within 10 to 20 $\mathrm{cm^{-1}}$ of the experimental anharmonic values. For ClOOCl, the calculated frequencies show somewhat larger differences of 20−25 $\mathrm{cm^{-1}}$ as compared to experiment[40] and a difference of ~60 $\mathrm{cm^{-1}}$ for the second *a* frequency mode. This is due to the fact that the bond distances are in error by 0.01−0.02 Å and that the Cl−O and O−O stretching coordinates are tightly coupled. The frequencies for ClOClO are in good agreement with the available experimental values, within 25 $\mathrm{cm^{-1}}$ for most bands. The calculated frequencies for OClO[45] ClOCl,[46] ClO,[44] and Cl_2[44] show the same excellent agreement with the experimental values as found for $ClClO_2$.

TABLE 1: Calculated Heats of Formation (kcal mol^{-1}) at 0 and 298 K[a]

Molecule	ΔH_f (0 K)$_{\mathrm{calc}}$	ΔH_f (298 K)$_{\mathrm{calc}}$	Reference ΔH_f (298 K)
ClOOCl	32.9	31.6	30.5 ± 0.7, 31.3 ± 0.7[b]
ClOClO	41.0	39.9	41.9
$ClClO_2$	29.4	28.5	36.9[c]
OClO ($^2B_1$)	24.5	23.9	22.6 ± 0.3, 23.53 ± 0.24[d]
ClOCl	19.3	18.9	19.4 ± 0.4
ClClO ($^1A'$)	32.2	31.9	22 ± 7
ClClO ($^3A''$)[e]	52.2	52.4	
ClO[f]	24.8	24.8	24.29 ± 0.03
Cl_2	−0.2	−0.2	0.0

[a] Experimental heats of formation were taken from ref 10 unless noted. [b] Reference 49. [c] Estimated from calculated values in ref 23 and ΔH_f (ClOOCl). [d] Reference 48. [e] MP2/aug-cc-pV(T+d)Z frequencies. [f] Includes molecular and atomic spin−orbit corrections.

The calculated heats of formation are given in Table 1. The results for the diatomics Cl_2 and ClO are within 0.5 kcal/mol of the experimental values.[47] For the triatomics ClOCl and OClO, the calculated heats of formation are also within 0.5 kcal/mol of experiment[47] if the most recent value of 23.53 ± 0.24 kcal/mol from the photodissociation dynamics study of Davis and Lee[48] is used for OClO; this value for OClO also agrees with the older JANAF value.[47]

For ClOOCl, the calculated heat of formation is 1.1 kcal/mol higher than the experimental value from Sander and coworkers,[4] which has an error bar of 0.7 kcal/mol. Our value for ClOOCl is in excellent agreement with the value of 31.3 ± 0.7 kcal/mol obtained by both Cox and Hayman[7] and the recent photoionization study by Plenge et al.[49] We note that the less positive experimental heats of formation of OClO and ClOOCl are from the same study[4] and appear to be off by 0.8−1.0 kcal/mol. Our results demonstrate that our calculated heats of formation should be accurate to ±1.0 kcal/mol, and we would expect the relative energies to be better than ±1 kcal/mol. The more approximate G2 value,[29] which includes empirical parameters for ΔH_f^{298}(ClOOCl), of 30.0 differs from our higher level value by 1.6 kcal/mol. G2 makes a comparable error in the ionization energy for ClOOCl as compared to experiment.

We predict that $ClClO_2$ is 3.1 kcal/mol more stable than ClOOCl at 298 K on the enthalpy scale and that $ClClO_2$ will be favored by an additional 0.8 kcal/mol on the free energy scale. There is a strong basis set dependence on the relative energy and one needs large basis sets to get this energy difference correct as shown in Table 2. It is not until the aug-cc-pVQZ basis is used that $ClClO_2$ becomes more stable than ClOOCl in terms of the electronic energy. At the G2 level,[29] $ClClO_2$ is predicted to be 6.8 kcal/mol less stable than ClOOCl in clear contradiction with our more accurate CBS results. Table 2 shows why the G2 calculations[29] make an error of 10 kcal/

TABLE 2: CCSD(T) Relative Electronic Energies for the Cl_2O_2 Isomers As a Function of Basis Set in kcal/mol

basis set	$\Delta E_{elec}(ClClO_2 \rightarrow ClOOCl)$	$\Delta E_{elec}(ClClO_2 \rightarrow ClOClO)$	$\Delta E_{elec}(ClOOCl \rightarrow ClOClO)$
aug-cc-pVDZ	−15.9	0.2	16.0
aug-cc-pVTZ	−1.4	9.7	11.2
aug-cc-pVQZ	1.7	11.4	9.7
aug-cc-pV5Z	3.4	12.4	9.1
CBS(Q5)	5.1	13.5	8.4

TABLE 3: Adiabatic Bond Dissociation Energies (kcal mol^{-1}) at 298 K

molecule	product	BDE
ClOOCl	ClO + ClO	18.0
	Cl + ClOO	20.8[a]
ClOClO	ClO + ClO	9.7
	Cl + OClO	13.0
	O + ClOCl	38.6
$ClClO_2$	Cl + OClO	24.4
	ClClO + O	63.0
OClO ($^2B_1$)	O + ClO	60.4
ClOCl	Cl + ClO	34.9
ClClO ($^1A'$)	O + Cl_2	27.6
	Cl + ClO	21.9
ClClO ($^3A''$)	O + Cl_2	7.2
	Cl + ClO	1.4
ClO ($^2\Pi$)	Cl + O	63.8
Cl_2	Cl + Cl	58.0

[a] Calculated using the experimental value for the heat of formation of ClOO from ref 50.

mol in the energy difference between ClOOCl and $ClClO_2$. G2 only does QCISD(T) with the singly polarized triple-ζ 6−311G(d,p) basis set which is approximately comparable to the aug-cc-pV(D+d)Z basis set. CCSD(T)/aug-cc-pV(D+d)Z clearly predicts the incorrect energy difference by 16 kcal/mol. Higher order basis set effects in G2 are included only at the MP2 and MP4 levels with polarized triple-ζ basis sets and even at the more accurate CCSD(T)/aug-cc-p(V+d)Z level, the $ClClO_2$ isomer is still less stable than ClOOCl. Thus G2 theory does not incorporate large enough basis sets to get this energy difference correct. The ClOClO isomer is predicted to be 8.3 kcal/mol above ClOOCl at 298 K and 11.4 kcal/mol above $ClClO_2$. The G2 value[29] for ΔH_f^{298}(ClOClO) is 2 kcal/mol higher than our value. Our results suggest that one must take care in the synthesis of ClOOCl to avoid the formation of $ClClO_2$, for example, on surfaces.

Our values can be used to predict the adiabatic bond dissociation energies (BDEs) of these species at 298 K in Table 3. The BDEs show that $ClClO_2$ is more stable with respect to bond breaking than is ClOOCl. In ClOOCl, the lowest BDE is for the O−O bond whereas in $ClClO_2$, the weakest BDE is for the Cl−Cl bond. The Cl−O BDE obtained using the experimental heat of formation for ClOO[50] in ClOOCl is slightly higher than the O−O BDE. ClOClO is expected to fragment by breaking the central O−Cl bond with a BDE of less than 10 kcal/mol. We also calculated the energy of the $^3A''$ state of ClClO. The stability of this state is very dependent on the quality of the basis set and that the aug-cc-p(5+d)Z basis set was required for this state to be stable. This state is 7.2 kcal/mol below the reactant O(^{3}P) + Cl_2 and 1.4 kcal/mol below the product state ClO + Cl consistent with the observation of a weak complex in molecular beam scattering experiments.[51] The singlet state of ClClO has much higher BDEs.

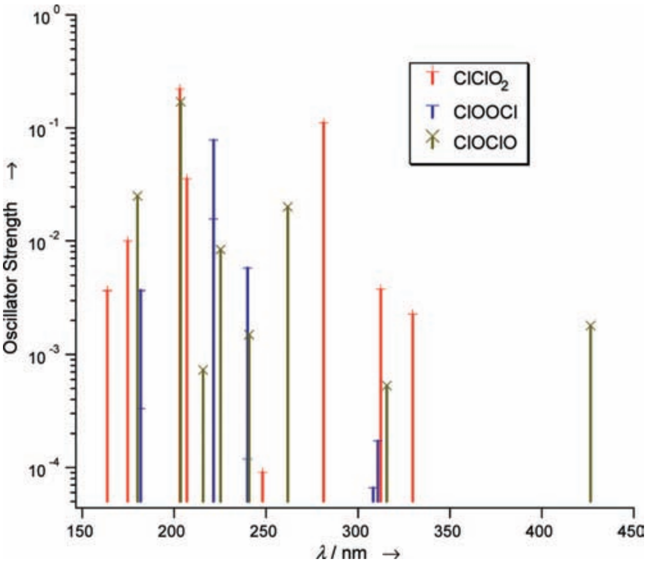

Figure 1. EOM-CCSD/aug-cc-pV(T+d)Z singlet excitation spectrum of $ClClO_2$, ClOOCl, and ClOClO.

TABLE 4: EOM-CCSD/aug-cc-pV(T+d)Z Excitation Energies (ΔE) and Oscillator Strengths (f) for $ClClO_2$, ClOOCl, and ClOClO at the aug-cc-pV(T+d)Z geometries

Molecule	state	ΔE (eV)	ΔE (nm)	f
$ClClO_2$	A^1A''	3.76	330	2.27×10^{-3}
	B^1A'	3.97	312	3.73×10^{-3}
	C^1A'	4.41	281	1.11×10^{-1}
	D^1A''	5.00	248	9.09×10^{-5}
	E^1A''	5.99	207	3.55×10^{-2}
	F^1A'	6.10	203	2.20×10^{-1}
	G^1A'	7.09	175	9.96×10^{-3}
	H^1A''	7.58	164	3.64×10^{-3}
ClOOCl	A^1B	3.99	311	1.72×10^{-4}
	B^1A	4.02	308	6.60×10^{-5}
	C^1B	5.17	240	5.75×10^{-3}
	D^1A	5.17	240	1.19×10^{-4}
	E^1B	5.60	221	7.81×10^{-2}
	F^1A	5.60	221	1.56×10^{-2}
	G^1B	6.82	182	3.32×10^{-4}
	H^1A	6.82	182	3.66×10^{-3}
ClOClO	A^1A	2.91	426	1.80×10^{-3}
	B^1A	3.93	315	5.28×10^{-4}
	C^1A	4.74	262	2.03×10^{-2}
	D^1A	5.15	241	1.51×10^{-3}
	E^1A	5.50	225	8.39×10^{-3}
	F^1A	5.75	216	7.26×10^{-3}
	G^1A	6.09	203	1.72×10^{-1}
	H^1A	6.89	180	2.51×10^{-2}

To provide information about the observations of the photoabsorption of ClOOCl, we calculated the vertical electronic excitation energies for ClOOCl, $ClClO_2$, and ClOClO at the EOM-CCSD/aug-cc-pV(T+d)Z level (EOM = equation of motion).[52] The spectra arising from the excited singlet states of all three species are shown in Figure 1 and summarized in Table 4. It should be noted that each of these states are characterized by single excitations from the ground state, hence EOM-CCSD should yield accurate results. This spectrum clearly demonstrates that singlet states of $ClClO_2$ absorb to longer wavelengths in the visible than do the singlet states of ClOOCl. Our calculated spectrum for $ClClO_2$ is consistent with that reported by Willner and co-workers,[40] who observed a UV spectra for $ClClO_2$ with maxima at 226 and 296 nm in the gas phase. We predict absorption peaks at 203 and 281 nm for the largest peaks, consistent with experiment. Our results are also consistent with the earlier calculations of Stanton and Bartlett on ClOOCl and $ClClO_2$[53] and of our previous calculations[55] on the excited states of ClOOCl. The ratio of the sum of the oscillator strengths of the two weak bands furthest to the red to the sum of the oscillator strengths of the next four bands for ClOOCl is <1:400. Assuming that the ratio of the oscillator strengths dominates the ratio of intensities, our results are in qualitative agreement with the results of the intensity ratios at 250 and 350 nm observed by Pope et al.,[5] which show a large value for this ratio in the range of 300. The oscillator strength for the most intense band in ClOOCl is predicted to be about a factor of 2.5 too high as compared to the experimental estimate[5] of 0.032 and the oscillator strength of the second most intense band is in excellent agreement with the experimental value[5] of 0.017. In addition, we predict that there is essentially no splitting between the A and B bands for a given excitation range as found experimentally for the most intense bands.[5] Calculations[28,54] at the complete active space-configuration interaction (CAS-CI) level do not show as good agreement with the CCSD results for ClOOCl. Previous workers[53−55] have noted that the lowest energy excitations for ClOOCl are into orbitals with predominately ClO σ^* character, which should facilitate dissociation into $\mathrm{Cl + OOCl}$, the main path observed experimentally. These results are also consistent with the CAS direct dynamics calculations,[28] which show formation of $\mathrm{2Cl + O_2}$.

The higher energy isomer, ClOClO is predicted to have a weak absorption in the visible at 427 nm, leading to breaking the ClO−ClO bond. We predict that the first excited state of ClOClO leading to Cl−OClO bond breaking is the one at 240 nm. The ClOClO isomer has been identified in Ar and Ne matrices by its infrared spectrum and visible light photolysis of $\mathrm{ClClO_2}$ in the Ar matrix has been shown to lead to formation of ClOClO.[40] Photolysis of ClOClO in an Ar matrix with visible light has also been shown to occur.[40]

It has previously been predicted[55] that that there are two triplet states >300 nm in ClOOCl at 389 and 385 nm on the basis of linear response CCSD calculations.[56] We predict triplet states >300 nm at 515, 382, and 350 nm for $\mathrm{ClClO_2}$ and at 527, 399, and 355 nm for ClOClO using the same approach with the aV(T+d)Z basis set. The oscillator strengths of the triplet states of ClOOCl and $\mathrm{ClClO_2}$ were calculated at the CASSCF level using the full Breit−Pauli spin orbit operator in the linear response CASSCF calculations with the aVTZ (ClOOCl)[55] and aV(T+d)Z ($\mathrm{ClClO_2}$) basis sets respectively using the Dalton program suite.[57,58] The oscillator strength of the more intense (of the two lowest lying triplets) $\mathrm{a^3B}$ transition for ClOOCl is about an order of magnitude less than that of the more intense (of the two lowest lying singlets) $\mathrm{A^1B}$ transition at the CASSCF level.[55] The low lying triplet state has been shown to smoothly dissociate to $\mathrm{Cl + ClOO}$.[55] Thus, in the region >370 nm for ClOOCl, the triplet state could be the most intense contributor to the photodissociation of ClOOCl as the peak of the lowest lying singlet is predicted to be at 310 nm. The oscillator strengths for $\mathrm{ClClO_2}$ for the three lowest energy transitions are 7.0×10^{-8} (^{3}A′, 515 nm), 5.5×10^{-5} (^{3}A″, 382 nm), and 1.5×10^{-4} (^{3}A′, 350 nm) in comparison to the values of 5.5×10^{-6} (^{3}B, 389 nm) and 1.5×10^{-5} (^{3}A, 385 nm) for ClOOCl. The most intense low lying triplet transition in $\mathrm{ClClO_2}$ has an oscillator strength that is almost an order of magnitude more intense than that in ClOOCl.

In summary, we predict that of the three low energy isomers of $\mathrm{Cl_2O_2}$, the $\mathrm{ClClO_2}$ isomer is the most stable and not the widely accepted ClOOCl isomer. An examination of the excited states of ClOOCl shows that there are only two weak absorption bands to the red of 245 nm at about 310 nm. This is consistent with the recently reported spectrum[5] of ClOOCl which shows much lower intensities in the tail to the visible than previously reported. Our results show that the $\mathrm{ClClO_2}$ isomer is a significant absorber in the near UV region and its potential presence needs to be accounted for in experiments. In particular it has two significantly more absorbing bands to the red of the lowest absorption band of ClOOCl. Our results provide new insights into the properties of the ClOClO isomer.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences, and the National Science Foundation for funding. D.A.D. thanks the Robert Ramsay Fund at the University of Alabama for partial support. We thank Dr. Stanley P. Sander of the Jet Propulsion Laboratory for many helpful discussions and comments.

Supporting Information Available: CCSD(T)/aV(T+d)Z optimized geometries for $\mathrm{Cl}_x\mathrm{O}_y$. CCSD(T)/aV(Q+d)Z oprimized geometries for $\mathrm{Cl_2O_2}$ isomers. Predicted and experimental vibrational frequencies, total CCSD(T)/aV(n+d) electronic energies as a function of basis set in au, and components for calculating the atomization energies in kcal mol^{-1} for $\mathrm{Cl}_x\mathrm{O}_y$. Linear response CCSD/aug-cc-pV(T+d)Z triplet excitation energies (ΔE) for $\mathrm{Cl_2O_2}$ isomers. Figures of the CCSD(T)/aV(T+d)Z optimized structures for $\mathrm{Cl}_x\mathrm{O}_y$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Molina, M. J.; Rowland, F. S. *Nature* **1974**, *249*, 810.

(2) von Hobe, M.; Salawitch, R. J.; Canty, T.; Keller-Rudek, H.; Moortgat, G. K.; Grooss, J.-U.; Muller, R.; Stroh, F. *Atmos. Chem. Phys.* **2007**, *7*, 3055.

(3) Molina, L. T.; Molina, M. J. *J. Phys. Chem.* **1987**, *91*, 433.

(4) Nickolaisen, S. L.; Friedl, R. R.; Sander, S. P. *J. Phys. Chem.* **1994**, *98*, 155.

(5) Pope, F. D.; Hansen, J. C.; Bayes, K. D.; Friedl, R. R.; Sander, S. P. *J. Phys. Chem. A* **2007**, *111*, 4322.

(6) Burkholder, J. B.; Orlando, J. J.; Howard, C. J. *J. Phys. Chem.* **1990**, *94*, 687.

(7) Cox, R. A.; Hayman, G. D. *Nature* **1988**, *332*, 796.

(8) Huder, K. J.; DeMore, W. B. *J. Phys. Chem.* **1995**, *99*, 3905.

(9) DeMore, W. B.; Tschuikow-Roux, E. *J. Phys. Chem.* **1990**, *94*, 5856.

(10) Bloss, W. J.; Nickolaisen, S. L.; Salawitch, R. J.; Friedl, R. R.; Sander, S. P. *J. Phys. Chem. A* **2001**, *105*, 11226.

(11) Wahner, A.; Tyndall, G. S.; Ravishankara, A. R. *J. Phys. Chem.* **1987**, *91*, 2734.

(12) Sander, S. P.; Friedl, R. R.; Ravishankara, A. R.; Golden, D. M.; Kolb, C. E.; Kurylo, M. J.; Huie, R. E.; Orkin, V. L.; Molina, M. J.; Moortgat, G. K.; Finlayson-Pitts, B. J. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies: Evaluation Number 14*; JPL Publication 02-25; National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology: Pasadena, CA, 2003.http://jpldataeval.jpl.nasa.gov/pdf/JPL_02-25_rev02.pdf.

(13) von Hobe, M. *Science* **2007**, *318*, 1878.

(14) Bartlett, R. J.; Musial, M. *Rev. Mod. Phys.* **2007**, *79*, 291.

(15) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803.

(16) (a) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Kendell, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(17) (a) Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484. (b) Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X.; Ng, C.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727. (c) Dixon, D. A.; Feller, D.; Peterson, K. A. *J. Chem. Phys.* **2001**, *115*, 2576. Pollack, L.; Windus, T. L.; de Jong, W. A.; Dixon, D. A. *J. Phys. Chem. A* **2005**, *109*, 6934.

(18) Peterson, K. A.; Shepler, B. C.; Figgen, D.; Stoll, H. *J. Phys. Chem. A* **2006**, *110*, 13877.

(19) McGrath, M. P.; Clemitshaw, K. C.; Rowland, F. S.; Hehre, W. J. *Geophys. Res. Lett.* **1988**, *15*, 883.

(20) Müller, H. S. P.; Willner, H. *Inorg. Chem.* **1992**, *31*, 2527.

(21) McKeachie, J. R.; Apple, M. R.; Kirchner, U.; Schindler, R. N.; Benter, Th. *J. Phys. Chem. B* **2004**, *108*, 16786.

(22) Pursell, C. J.; Conyers, J.; Denison, C. *J. Phys. Chem.* **1996**, *100*, 15450.

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

(24) Müller, H. S. P.; Cohen, E. A.; Christen, D. *J. Chem. Phys.* **1999**, *110*, 11865.

(25) Zhu, R. S.; Lin, M. C. *J. Chem. Phys.* **2003**, *118*, 4094.

(26) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(27) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(28) Kaledin, A. L.; Morokuma, K. *J. Chem. Phys.* **2000**, *113*, 5750.

(29) Li, W.-K.; Ng, C.-Y. *J. Phys. Chem. A* **1997**, *101*, 113.

(30) (a) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219. (b) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321.

(31) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.

(32) (a) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639. (b) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.

(33) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669.

(34) (a) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89. (b) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756. (c) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742. (d) de Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48. EMSL basis set library. http://www.emsl.pnl.gov/forms/basisform.html.

(35) (a) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(36) Moore, C. E. Atomic energy levels as derived from the analysis of optical spectra, Volume 1, H to V; U.S. National Bureau of Standards Circular 467, COM-72-50282, U.S. Department of Commerce, National Technical Information Service: Washington, D.C., 1949.

(37) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(38) Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Knowles, P. J.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Werner, H.-J. *MOLPRO a package of ab initio programs*, version 2002.6; Werner, H.-J.; Knowles, P. J., designers; http://www.molpro.net.

(39) DALTON, a molecular electronic structure program, Release 2.0 (2005), see http://www.kjemi.uio.no/software/dalton/dalton.html.

(40) Jacobs, J.; Kronberg, M.; Müller, H. S. P.; Willner, H. *J. Am. Chem. Soc.* **1994**, *116*, 1106.

(41) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2003**, *107*, 9641.

(42) Kuchitsu, K. Ed. *Landolt-Bornstein: Group II: Atomic and Molecular Physics, Volume 21: Structure of Free Polyatomic Molecules - Basic Data*, Springer-Verlag: Berlin, 1998.

(43) Sugie, M.; Ayabe, M.; Takeo, H; Matsumura, C. *J. Mol. Struct.* **1995**, *352/353*, 259. Herberick, G. E.; Jackson, R. H.; Millen, D. J. *J. Chem. Soc.* **1966**, 1156. Nakata, M.; Sugie, M.; Takeo, H.; Matsumura, C.; Kuchitsu, K. *J. Mol. Spectrosc.* **1981**, *86*, 241. Jackson, R. H.; Millen, D. J. *Proc. Chem. Soc.* **1967**, *10*, 1157.

(44) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules. Molecular Spectra and Molecular Structure, Vol. IV*, Van Nostrand: Princeton, 1979.

(45) (a) Müller, H. S. P.; Willner, H. *J. Phys. Chem.* **1993**, *97*, 10589. (b) Esposito, A. P.; Stedl, T.; Jonsson, H.; Reid, P. J.; Peterson, K. A. *J. Phys. Chem. A* **1999**, *103*, 1748.

(46) Shimanouchi, T. Tables of Molecular Vibrational Frequencies Consolidated Volume I, NSRDS-NBS 39, National Bureau of Standards: Washington, D.C., 1972.

(47) Chase, M. W., Jr. *NIST-JANAF Thermochemical Tables, Fourth Edition, J. Phys. Chem. Ref. Data*, Monograph 9, **1998**, 1.

(48) Davis, H. F.; Lee, Y. T. *J. Chem. Phys.* **1996**, *105*, 8142.

(49) Plenge, J.; Kühl, S.; Vogel, B.; Müller, R.; Stroh, F.; von Hobe, M.; Flesch, R.; Rühl, E. *J. Phys. Chem. A* **2005**, *109*, 6730.

(50) (a) Nicovich, J. M.; Kreutter, K. D.; Shackelford, C. J.; Wine, P. H. *Chem. Phys. Lett.* **1991**, *179*, 367. (b) Baer, S.; Hippler, H.; Rahn, R.; Siefke, M.; Seitzinger, N.; Troe, J. *J. Chem. Phys.* **1991**, *95*, 6463. (c) Maudlin, R. L., III; Burkholder, J. B.; Ravishankara, A. R. *J. Phys. Chem.* **1992**, *96*, 2582.

(51) (a) Parrish, D. D.; Herschbach, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 6133. (b) Gorry, P. A.; Nowikow, C. V.; Grice, R. *Mol. Phys.* **1979**, *37*, 347.

(52) Korona, T.; Werner, H.-J. *J. Chem. Phys.* **2003**, *118*, 3006.

(53) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 9335.

(54) Toniolo, A.; Persico, M.; Pitea, D. *J. Phys. Chem. A* **2000**, *104*, 7278.

(55) Peterson, K. A.; Francisco, J. S. *J. Chem. Phys.* **2004**, *121*, 2611.

(56) Christiansen, O.; Koch, H.; Halkier, A.; Jørgensen, P.; Helgaker, T.; Meras, A. S. D. *J. Chem. Phys.* **1996**, *105*, 6921.

(57) Olsen, J.; Jørgensen, P. in Modern Electronic Structure Theory, Yarkony, D. R. (Ed.) World Scientific: Singapore, 1995, Vol. 2, p. 857.

(58) Angeli, C.; Bak, K. L.; Bakken, V.; Christiansen, O.; Cimiraglia, R.; Coriani, S.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Fernandez, B.; Hättig, C.; Hald, K.; Halkier, A.; Heiberg, H.; Helgaker, T.; Hettema, H.; Jensen, H. J. Aa.; Jonsson, D.; Jørgensen, P.; Kirpekar, S.; Klopper, W.; Kobayashi, R.; Koch, H.; Ligabue, A.; Lutnæs, O. B.; Mikkelsen, K. V.; Norman, P.; Olsen, J.; Packer, M. J.; Pedersen, T. B.; Rinkevicius, Z.; Rudberg, E.; Ruden, T. A.; Ruud, K.; Sałek, P.; Sanchez de Meras, A.; Saue, T.; Sauer, S. P. A.; Schimmelpfennig, B.; Sylvester-Hvid, K. O.; Taylor, P. R.; Vahtras, O.; Wilson, D. J.; Ågren, H. DALTON Release 2, 2005. http://www.kjemi.uio.no/software/dalton/

JP806220R