Low-lying isomers of the chlorine oxide dimer: A theoretical study

4 AUTHORS:

John F Stanton
University of Texas at El Paso
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Magnus Rittby
Texas Christian University
86 PUBLICATIONS **2,406** CITATIONS

Rodney J. Bartlett
University of Florida
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Darin W Toohey
University of Colorado Boulder
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interesting aspects of these data. Figure 3 contains the Ne and Ar data plotted against ΔE. The display in Figure 3 is familiar. As with all the beam scattering conditions so far explored, the V–T inelastic scattering is well represented by the EGL.

Low-Lying Isomers of the Chlorine Oxide Dimer: A Theoretical Study

John F. Stanton,* **C. Magnus L. Rittby, Rodney J. Bartlett,**

Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32611
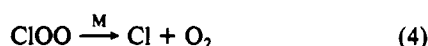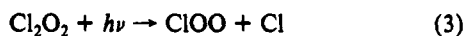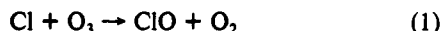
and Darin W. Toohey

Departments of Chemistry and Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts 02138 (Received: November 1, 1990)

Ab initio thermochemical stabilities have been calculated for three isomers of the dimer of chlorine oxide (ClO) with many-body perturbation theory (MBPT) and the infinite-order coupled-cluster (CC) approximation. Results indicate that chlorine peroxide (ClOOCl) is the most stable form of Cl_2O_2, although the alternative structure $Cl(ClO_2)$ cannot be definitively eliminated on the basis of the present calculations. Calculations of low-lying electronic excitation energies for ClOOCl and $Cl(ClO_2)$ with Fock-space multireference CC suggest that both isomers have transitions near 250 nm to energy levels that yield either free chlorine atoms or considerably weakened ClO bonds. Additional calculations for the dipole moment and quadrupole moments of chlorine peroxide are presented. In general, the results are in good agreement with experimental studies which show that ClOOCl is the predominant form of Cl_2O_2 in the laboratory and that its photolysis in the ultraviolet region yields two chlorine atoms, thus supporting theories of catalytic destruction of ozone by chlorine in the winter polar stratosphere.

Introduction

The photochemistry and thermochemistry of the dimer of chlorine oxide (ClO) have occupied center stage in the discussion of ozone loss in the earth's polar stratosphere since the discovery of the Antarctic "ozone hole".[1] The catalytic cycle shown in eqs 1–4, initiated by the self-association of ClO, not only has been

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

$$ClO + ClO + M \rightleftharpoons Cl_2O_2 + M \qquad (2)$$

$$Cl_2O_2 + h\nu \rightarrow ClOO + Cl \qquad (3)$$

$$ClOO \xrightarrow{M} Cl + O_2 \qquad (4)$$

invoked to explain both quantitatively and qualitatively the dramatic losses above Antarctica,[2] but also recently has been linked to ozone loss at high latitudes in the northern hemisphere.[3] However, several important questions remain regarding the structure, stability, formation, and subsequent photochemical behavior of Cl_2O_2 before we can establish conclusively the causal link between high concentrations of ClO and the observed ozone losses. Key assumptions in this ozone-destroying cycle under conditions which prevail in the polar stratosphere are (1) photolysis of Cl_2O_2 (followed by decomposition of ClOO) into chlorine atoms and O_2 rather than into ClO; and (2) a sufficient bond strength of Cl_2O_2 such that thermal decomposition back to reactants is less favorable than photolysis.

Molina and Molina[4] argued that there may be two straight-chain isomers of Cl_2O_2, ClOOCl and ClOClO, and that only photolysis of chlorine peroxide would yield the desired products.

The first ab initio investigations of these compounds suggested that ClOOCl was the more stable of the two by about 8 kcal/mol.[5] However, these results showed a strong dependence on the treatment of correlation energy, reflecting the difficulty single-reference theories have in treating these species. A similar study by McGrath et al.[6] added the bridged chloryl chloride ($ClClO_2$) to the list of candidate structures for Cl_2O_2 and found this species and the chlorine peroxide to be comparable in energy. From kinetic arguments, however, one might expect formation of this bridged species from ClO fragments to be unfavorable, as it requires formation of two bonds and breakage of a third.

Laboratory experiments have demonstrated that the kinetically favored form of Cl_2O_2 is indeed chlorine peroxide[7] and have yielded a structure with which the aforementioned theoretical predictions agree well. Thermal measurements under similar experimental conditions[8] indicate that the equilibrium bond strength is 17.5 ± 0.5 kcal/mol and UV/visible spectroscopic studies demonstrate that Cl_2O_2 is an efficient absorber of short-wavelength solar radiation[9] and that Cl atoms are the primary photolysis products at 308 nm.[10] However, these experiments do not exclude the possibility that other isomers of Cl_2O_2 may have important roles in the stratosphere where time scales are many orders of magnitude longer than those employed in the laboratory studies. Of considerable interest is the possibility that more stable forms of Cl_2O_2 with potentially different photochemical behavior may form by isomerization of the kinetically favored form.

Two recent theoretical studies have focused on Cl_2O_2 isomers,[6,11] and one of these[11] has addressed the issue of UV/visible absorption. Jensen and Oddershede applied the random phase approximation (RPA) to calculate the line positions and oscillator strengths of

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the low-lying electronic transitions of the three most likely structures of Cl_2O_2. They argued that the spectrum observed experimentally by a number of groups is due to the $ClClO_2$ isomer, and not to the peroxide, in disagreement with the experimental work summarized above. Very recently, Eberstein[12] concluded that chlorine peroxide will not photolyze to chlorine atoms at the photon energies near 250 nm, again contradicting recent experimental work of Molina et al.[10] Eberstein's argument, however, was based on an at best tenuous "analogy" between the photochemical properties of hydrogen peroxide and $ClOOCl$.

In light of the recent theoretical studies mentioned above—which cast doubt on the connection between high concentrations of ClO and polar ozone loss—we have carried out high-level theoretical calculations on the thermochemical stabilities and electronic excitation energies of chlorine oxide dimers. The results of these calculations, which were carried out with many-body perturbation theory (MBPT),[13] the infinite-order coupled-cluster (CC) approximation,[14] and multireference Fock-space CC methods,[15] are reported in this Letter.

Theoretical Methods

All of the calculations reported in this manuscript were performed with the ACES,[16] ACES II,[17] and GAUSSIAN[18] program systems. The geometries employed were the minimum energy MBPT(2)/6-31G* structures reported by McGrath et al.[6] Two basis sets were used in the single point energy calculations used to estimate the thermochemical stabilities. The first, hereafter referred to as basis A, is the double-zeta plus polarization set of Dunning and Hay,[19] which consists of 40 contracted Gaussian functions for each ClO unit. Since it is widely known that an accurate theoretical description of second-row atoms such as chlorine (particularly those in hypervalent environments) requires multiple polarization functions,[20] a very large Gaussian basis was also used. In this basis, which we shall call set B, the [5s3p2d] contracted described in ref 21 was used for oxygen. For chlorine, a [6s5p3d1f] set was constructed from the [6s5p] McLean–Chandler basis.[22] The polarization functions consisted of a best fit of two Gaussian functions to a Slater-type d orbital with exponent 3.358, and two additional singly contracted Gaussians with exponents of 0.375 and 0.1875. The exponent of the f function was chosen to be 0.7. Basis B, which consists of 75 contracted Gaussian functions per ClO unit, should provide an adequate description of the bonding in ClO dimers.

Correlation energies were evaluated for three isomers of the ClO dimer—the peroxide, chloryl chloride, and straight-chain ClOClO forms—with basis sets A and B at second-, third-, and fourth-order MBPT [MBPT(2), MBPT(3), and MBPT(4)], as well as with the partial fourth-order model known as SDQ-MBPT(4), which neglects the effects of triple excitations from

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TABLE I: Isomerization Energies (Peroxide → Cl_2O_2) and Symmetric Binding Energies (2ClO → Cl_2O_2) for Cl_2O_2 Isomers[a]

	ΔE(peroxide → Cl_2O_2)		ΔE(2ClO → Cl_2O_2)	
	basis A	basis B	basis A	basis B
Chlorine Peroxide (ClOOCl)				
SCF	0.0	0.0	26.9	29.9
MBPT(2)	0.0	0.0	−35.1	−34.3
SDQ-MBPT(4)	0.0	0.0	−22.5	−19.5
MBPT(4)	0.0	0.0	−28.2	−28.4
CCSD	0.0	0.0	−17.1	
CCSD + T(CCSD)	0.0	0.0	−20.6	
Chloryl Chloride (ClClO$_2$)				
SCF	64.0	33.7	90.9	63.5
MBPT(2)	31.4	−4.5	−3.7	−38.8
SDQ-MBPT(4)	45.1	13.7	22.6	−5.9
MBPT(4)	31.7	−1.5	3.5	−30.0
CCSD	49.8		32.7	
CCSD + T(CCSD)	39.9		19.3	
Chlorine Chlorite (ClOClO)				
SCF	43.3	31.3	70.2	61.2
MBPT(2)	22.5	8.6	−12.6	−25.7
SDQ-MBPT(4)	14.7		7.8	
MBPT(4)	23.2		−5.0	
CCSD	32.7		15.6	
CCSD + T(CCSD)	25.3		4.8	

[a] All values in kcal/mol.

the reference determinant. To estimate the importance of infinite-order effects, CC calculations were performed with basis A for all isomers at the coupled-cluster singles and doubles level (CCSD) and also with the CCSD + T(CCSD) model, which includes an additional correction for triple excitation effects. Determinants corresponding to excitation from the core level molecular orbitals ($n = 1$ for oxygen, $n = 1$ and 2 for chlorine) were excluded from the configuration space used in the correlation energy calculations, resulting in 13 active occupied orbitals and 55 active virtual orbitals for basis A (125 for B).

Electronic excitation energies were calculated by using Fock-space multireference coupled-cluster (MRCC) theory,[15] including one- and two-body cluster operators. This method is both computationally efficient and powerful. All excitation energies are obtained in a single calculation, and MRCC generates proper correlated CC ground and excited states. This should be distinguished from the RPA method that implicitly assumes that the ground state can be described by a single reference function. In addition, MRCC is not plagued by the triplet instability problem, although the latter shortcoming of RPA did not affect the results of ref 11 since they studied only singlet excitation energies. Since the MRCC method is quite new, it is not as well calibrated as most of our other techniques, but prior experience has shown that good agreement with experiment is obtained even for difficult multireference cases such as ozone, and other molecules including *sym*-tetrazine and diazomethane.[23]

Results and Discussion

In Table I, relative energies of the three Cl_2O_2 isomers studied by McGrath et al. are presented, as well as the respective electronic dissociation energies to two ground-state ClO molecules. Since basis A contains only a single polarization function on the chlorine atom, it appears to grossly underestimate the stability of the two isomers with hypervalent chlorine atoms—the straight-chain ClOClO isomer (chlorine chlorite) and the bridged chloryl chloride structure—at all levels of theory. What is significant about these results is the obvious importance of infinite-order effects and triple excitations in determining the relative stabilities of the isomers. For many chemical systems, fourth-order MBPT provides an adequate description, and SDQ-MBPT(4) and MBPT(4) properties do not deviate significantly from their infinite-order counterparts [CCSD and CCSDT, the latter approximated in the

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TABLE II: Estimated Dissociation Energies ($Cl_2O_2 \rightarrow 2ClO$) of Chlorine Peroxide Isomers[a]

	ClOOCl	ClClO$_2$
ΔE(electronic)	20.75	14.14
vibrational zero-point correction	−1.83	−2.94
ΔE(0 K)	18.92	11.17

[a] Values are obtained from applying the infinite order contributions evaluated with basis A to the MBPT(4) results obtained with basis B. All energies in kcal/mol.

present research by the CCSD + T(CCSD) model].[14] This is not the case here. It appears that infinite-order effects favor the peroxide relative to the other two isomers by approximately 10 kcal/mol and that they are also important in determining the dimerization energy of ClO. This is largely due to significant multireference character in both of the hypervalent structures and the ClO radical. Although the related molecule FOOF is notoriously difficult to describe theoretically due to the strong multireference effects arising from the "normal" resonance structure and that with O–F double bonds,[24] chlorine peroxide is relatively well described by a single determinant, presumably due to poor π overlap between chlorine and oxygen. The largest amplitude corresponding to an excited electronic configuration in the CCSD wave function of ClOOCl is only 0.05, while amplitudes of magnitude 0.10 and higher are typically found in difficult molecules. In contrast, both of the hypervalent isomers have double excitation amplitudes which are more than twice as large (0.12 for ClOClO and 0.18 for ClClO$_2$), while ClO has a single excitation amplitude of 0.17. The latter two values are comparable to those obtained for ozone, which is also poorly characterized by finite-order MBPT models.[25] For difficult cases such as these, correlation corrections to properties and relative energies tend to be oscillatory, and fourth order often overestimates these effects, as observed here.

As expected, expansion of the basis from A to B favors the hypervalent forms. At the MBPT(2) level, both ClOClO and chloryl chloride have energies comparable to the peroxide, with the latter actually 4.5 kcal/mol lower. Higher level calculations were not carried out for ClOClO because of the large number of molecular orbital integrals for this molecule, due to its lower symmetry. Nevertheless, the second-order energy for this molecule together with the qualitative order-by-order behavior found for basis A suggests that this form is as much as 10 kcal/mol less stable than the peroxide. At the full MBPT(2) and MBPT(4) levels, the chloryl chloride is actually lower in energy than the peroxide. However, as mentioned above, the MBPT(4) model can overestimate the contribution of electron correlation to the stability, and it is likely that the peroxide is the most stable form by about 5 kcal/mol with this basis.

Application of the infinite-order corrections obtained with basis A to the SDQ-MBPT(4) and MBPT(4) dissociation energies provides a reasonable approximation to the basis B-CCSD and basis B-CCSD + T(CCSD) values for ClOOCl and ClClO$_2$. Dissociation energies obtained in this way are presented in Table II, along with the vibrational zero-point-energy corrections computed from the harmonic frequencies of McGrath et al. for Cl_2O_2 isomers and the fundamental frequency of ClO given by Basco and Morse.[26] The resulting zero-point-corrected *approximate* CCSD + T(CCSD) dissociation energies are 11.2 kcal/mol for chloryl chloride and 18.9 kcal/mol for chlorine peroxide. These values, which are not derived from a single calculation but represent an educated guess based on basis set and infinite-order effects, carry an uncertainty of roughly 3–5 kcal/mol for ClOOCl and somewhat more for chloryl chloride because of its hypervalency and multireference character. It should be noted that the

TABLE III: Lowest Singlet Excitation Energies of Chlorine Peroxide (ClOOCl) and Chloryl Chloride (ClClO$_2$), Calculated with Fock-Space Multireference Coupled-Cluster Theory Using Basis A and RPA Results of Ref 11

| upper state sym | ΔE(vertical) | | | |
| | FSMRCC | | RPA | |
	eV	nm	eV	nm
	Chlorine Peroxide (ClOOCl)			
B	3.73	332	4.23	293
A	3.76	330	4.27	290
A	5.04	246	5.51	225
B	5.04	245	5.49	226
A	5.43	228		
	Chloryl Chloride (ClClO$_2$)			
A″	2.17	571	2.58	481
A′	2.24	554	2.62	473
A′	3.47	358	3.46	358
A″	3.74	332	4.20	295
A″	4.50	276	5.54	224
A′	4.81	258	5.10	243

TABLE IV: Components of the Dipole and Quadrupole Moments of Chlorine Peroxide, Calculated at the SCF and MBPT(2) Levels with the 118-GTO Basis Set Described in the Text[a]

property	SCF	MBPT(2)
μ_z, D	1.05	0.82
θ_{xx}, au	−1.90	−1.66
θ_{yy}, au	2.48	2.07
θ_{xy}, au	−1.05	−0.84

[a] The principal axis system is used, with the C_2 rotational axis coincident with z.

value of 18.9 kcal/mol for ClOOCl is in good agreement with the experimental measurement of 17.5 kcal/mol reported in ref 8.

Low-lying electronic excitation energies for chloryl chloride and chlorine peroxide were predicted with the MRCC method and are presented in Table III. The excitation energies predicted with MRCC are systematically shifted to longer wavelengths than the RPA values for both molecules, with typical disagreements of about 0.5 eV but as much as 1 eV for one of the values for chloryl chloride. The calculations suggest that both forms of the ClO dimer will have electronic absorptions near 250 nm, with ClClO$_2$ absorbing at a slightly longer wavelength than the peroxide. The effective Hamiltonian eigenvectors show strong orbital mixing, suggesting that a single-reference based method such as RPA is less adequate to describe these excitations. Nevertheless, examination of the eigenvectors reveals that the best molecular orbital description of all of the low-energy excitation processes involves the population of Cl–O σ antibonding orbitals, suggesting that *photolysis of either isomer near 250 nm will lead to either a free chlorine atom or a considerably weakened Cl–O bond.*

As stated in the Introduction, Eberstein[12] has recently concluded that photolysis of chlorine peroxide at these wavelengths cannot lead to the liberation of a free chlorine atom. His contention, however, is based on an "analogy" between chlorine peroxide and hydrogen peroxide. By applying an empirical correction of 100 nm to the absorption spectrum of HOOH, he concludes that the photodissociation of ClOOCl to a free chlorine atom will not occur to the red of 223 nm. Rather, he suggests, absorption of long-wavelength photons will lead to cleavage of the O–O bond since it is the weakest bond in the molecule. Our calculations, however, indicate that cleavage of the O–Cl bond may occur at energies as low as 330 nm. Furthermore, examination of our results shows that upper state population of O–O antibonding orbitals does not occur for *any* excitation above 200 nm. Although Eberstein dismisses Molina and Molina's discussion[4] of the qualitative nature of the photodissociation process as "highly speculative", their suggestion that the process involves promotion of a chlorine nonbonding electron to a Cl–O antibonding orbital now seems perceptive, as it is borne out in our Fock-space calculations which indicate that both of the excitations near 250 nm are well described by this model. On the basis of the results presented above, we

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feel that the conclusion of Eberstein that ClOOCl will not dissociate to ClO₂ and a free chlorine atom at wavelengths above 220 nm is probably not correct.

Finally, we have carried out calculations of the dipole and quadrupole moments of the chlorine peroxide isomer at the MBPT(2) level, using a 118-GTO basis set derived from basis B by deleting the outermost d and f orbitals on chlorine. These calculations were carried out analytically, using the relaxed density formalism of Salter, Trucks, and Bartlett.[27] Since ClOOCl is relatively well described by a single reference determinant, the values presented in Table IV should be quite accurate, with the dipole moment likely to fall within a few tenths of a debye of the exact value. Since we believe that ClOOCl is the most stable form of Cl_2O_2, we present these results in the hope that they will assist experimentalists in further verification of the existence of ClOOCl.

Conclusions

Perhaps the most important conclusion to be drawn from the present study is that the Cl_2O_2 isomers, particularly the hypervalent straight-chain ClOClO form and chloryl chloride, are extremely difficult to study theoretically. In fact, the strong infinite-order effects observed in the study of the relative stabilities of these forms suggest that any results obtained with finite-order MBPT (also known as Moller–Plesset or MP perturbation theory) models for these isomers *should not be regarded as quantitative* by experimentalists who seek stabilities to better than 1 kcal/mol. Meaningful properties and relative energies for these systems *must* be determined with models including infinite-order effects, such as the coupled-cluster approximation, or even multireference correlated treatments. For example, the multireference nature of ClClO₂ is comparable to that of ozone. Consequently, the MBPT(2) harmonic frequencies and infrared intensities for this molecule presented by McGrath et al.[6] may be no more reliable than are those for ozone. The harmonic force field of ozone has recently become a popular benchmark for quantum chemical methods.[25,28] It has been shown by this group and others that finite-order MBPT models do an extremely poor job of predicting the harmonic frequencies of ozone, with the widely used MBPT(2) model overestimating the frequency of the antisymmetric stretching mode by more than 1000 cm⁻¹. Therefore, in the absence of higher level calculations or definitive experimental observations, one must be ready to assume that the MBPT(2) force field of ClClO₂ is no better than that for ozone. The same is true

for the ClOClO form, while the MBPT(2) force field for ClOOCl is probably fairly accurate.

Similarly, the oscillator strengths presented by Jensen and Oddershede[11] may also have large uncertainties since the RPA method is only reliable for single-reference cases. The strong state mixing observed in our MRCC studies suggests that the RPA method may not provide a good description of the excitation process. It is unlikely, however, that the oscillator strength for the ClOOCl excitation near 250 nm is larger than that for ClClO₂ since the RPA values differ by 3 orders of magnitude and are probably not qualitatively in error. Calculation of the oscillator strength using more sophisticated models is an important area for further calculations and will be carried out with the FSMRCC method after this capability has been implemented.

Summary

Although the calculations of excitation energies and relative stabilities of Cl_2O_2 isomers presented here are by far the most extensive yet carried out on this system, they are still not conclusive. Quantum chemical calculations alone are still a long way from solving the problem of the Antarctic ozone hole. The difficult nature of the Cl_2O_2 systems necessarily demands high-level infinite-order treatment of electron correlation and very large basis sets. We have succeeded only in showing that the peroxide is *most likely* the lowest energy structure with a predicted dissociation energy in good agreement with accurate experimental values. Furthermore, we have demonstrated that the ClOOCl and ClClO₂ isomers can absorb UV radiation near 250 nm and that the upper state in each case involves the population of a Cl–O antibonding orbital. This latter finding contradicts the assumption of Eberstein[12] regarding the photodissociation of ClOOCl and therefore vitiates his argument regarding the photodissociation products in the near-UV region. Consequently, high-level quantum chemical calculations do not rule out the importance of the role of ClO in polar ozone depletion. Perhaps most important, our studies agree well with the laboratory studies which show that ClOOCl is the major (if not the sole) product of ClO recombination at temperatures and pressures characteristic of the polar stratosphere.[7] In addition, they provide added confidence to studies which find chlorine atoms (and ClOO, which subsequently decomposes to Cl and O₂) to be the major products of Cl_2O_2 photolysis[10] and to in situ observations of ClO which indicate that ClOOCl is the nighttime reservoir of ClO in the wintertime polar stratosphere.[29]

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Sign of Circular Dichroism Induced by β-Cyclodextrin

Masato Kodaka

National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan (Received: November 2, 1990)

On the basis of the coupled oscillator theory, the circular dichroism induced by β-cyclodextrin (β-CDx) is calculated. It is revealed from the calculation that outside the cavity of β-CDx the sign of the induced circular dichroism (ICD) becomes opposite to that inside it; namely, outside the cavity of β-CDx an electric transition polarized along the axis of the cavity gives negative ICD while a transition polarized normal to it affords positive ICD. The present rule is supported qualitatively in view of the dipole–dipole interaction between a transition moment of a chromophore and an individual bond in β-CDx.

Introduction

Induced circular dichroism (ICD) has been frequently utilized to obtain the orientation of an aromatic molecules involved in cyclodextrin (CDx)[1–9] or to determine the direction of a transition

moment of a chromophore.[10,11] Using the Kirkwood–Tinoco expression based on the coupled oscillator theory,[12] Harata et al.[1]

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