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Gaussian-2 *ab Initio* Study of Isomeric Cl_2O_2 and $Cl_2O_2^+$ and Their Dissociation Reactions

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The energetics for Cl_2O_2 isomers and their cations as well as the fragments of these species have been investigated at the Gaussian-2 level of *ab initio* theory. It is found that the calculated heats of formation and dissociation energies for Cl_2O_2 and $Cl_2O_2^+$ isomers, as well as the ionization energies of the neutral species, are in good agreement with available experimental measurements. In addition, on the basis of these computational results, it may be concluded that both ClOOCl and ClOClO are formed in the dimerization of ClO.

Introduction

Chlorine oxide, ClO, is believed to play a role in the ozone depletion over the Antarctic in springtime, and it is generally assumed the destruction of ozone occurs via a catalytic cycle involving a dimer of chlorine oxide, Cl_2O_2.[1] This understanding has prompted many experimental and theoretical studies on the chemistry and physical properties of isomeric Cl_2O_2 and their fragments. On the experimental side, thermodynamic properties of gaseous ClOOCl and its fragments have been determined.[2] In addition, the ionization energies of ClO and Cl_2O_2 have been reported recently.[3] Theoretical investigations include studies on the structures, relative stabilities, and vibrational spectra of Cl_2O_2 isomers,[4] UV spectra of Cl_2O_2 isomers,[1] density functional theory calculations of ClOO,[5] and coupled cluster calculations of the potential energy surface and spectroscopic constants of ClO_2^+,[6] etc. In the present work, we carry out Gaussian-2 (G2) calculation for the isomeric Cl_2O_2 and $Cl_2O_2^+$ and their fragments to obtain their heats of formation at 0 and 298 K (ΔH°_{f0} and ΔH°_{f298}) and the ionization energies (IE's) of the neutral species. Also, energies of the various dissociation reactions involving isomeric Cl_2O_2 and $Cl_2O_2^+$ have also been calculated. Where possible, a comparison between the calculated quantities and experimental data is made.

Theoretical Methods and Results

All calculations were carried out on RS6000/390 and SGI8000 workstations using the Gaussian 94 package of programs.[7] The molecular structures for all species were optimized using the second-order Mϕller−Plesset theory (MP2) with the 6-31G(d) basis set, and all electrons were included at the MP2(full)/6-31G(d) level. The MP2(full)/6-31G(d) structures were then employed for energy calculations according to the G2 procedure.[8] The only exception is that we were not able to obtain an optimized structure for $ClOOCl^+$ at the MP2(full)/6−-31G(d) level after many attempts. Hence, for the G2 calculation of this cation, we used the HF/6-31G(d) structure instead. The optimized structures of Cl_2O_2 isomers have already been reported.[4] Those of $Cl_2O_2^+$ isomers are summarized in Table 1.

TABLE 1: Optimized Structural Parameters for $Cl_2O_2^+$ Isomers (Bond Distances in Å and Angles in deg)[a]

cation	structural parameters
$ClOOCl^+$ (C_{2h})	Cl−O, 1.698; O−O, 1.261; Cl−O−O, 111.1
$ClClO_2^+$ (C_s)	Cl−Cl, 3.275; Cl−O, 1.459; Cl−Cl−O, 96.9; O−Cl−O, 121.5
$ClOCl'O'^+$ (C_1)	Cl−O, 1.742; O−Cl′, 1.645; Cl′−O′, 1.512; Cl−O−Cl′, 113.8; O−Cl′−O′, 111.6; Cl−O−Cl′−O′, 79.9

[a] The structure of $ClOOCl^+$ was optimized at the HF/6-31G(d) level, while those of $ClClO_2^+$ and $ClOClO^+$ were optimized at the MP2(full)/6-31G(d) level.

The G2 theoretical procedure[8] involves single-point total energy calculations at the MP4/6-311G(d,p), QCISD(T)/6-311g(d,p), MP4/6-311+G(d,p), MP4/6-311G(2df,p), and MP2/6-311+G(3df,2p) levels. A small empirical correction is employed to include the high-level correlation effects in the calculations of the total electronic energies (E_e). The HF/6-31G(d) harmonic vibrational frequencies, scaled by 0.8929, are applied for zero-point vibrational energy (ZPVE) corrections to obtain the total energies 0 K ($E_0 = E_e +$ ZPVE). The total enthalpies at 298 K (H_{298}) for molecular species are calculated using the scaled HF/6-31G(d) harmonic frequencies.

Upon obtaining E_0 and H_{298} for Cl_2O_2 and Cl_2O_2 as well as their fragments, it is straightforward to calculate their ΔH°_{f0} and ΔH°_{f298} and the IE values of the neutral species. These results are summarized in Table 2. In addition, using the E_0 values, the dissocaition energies (D_0's) of the various reactions involving isomeric Cl_2O_2 and their cations can be determined readily (see Table 3).

Before proceeding to discussing the results, it is noted that the G2 predictions for ΔH°_{f0}'s, ΔH°_{f298}'s, and IE's are usually within ±0.15 eV (or about ±15 kJ mol^{-1}) of the experimental data.[8] So far we have applied the G2 method to determine the ΔH°_{f0}'s of C_2H_5S isomers,[9] CH_3S_2,$^+$ CH_3S_2, and $CH_3S_2^-$ isomers,[10,11] CH_3O^+, CH_3O, and $CH_3O_2^-$ isomers,[12−14] SF_n^+, SF_n, and SF_n^-, $n = 1, 2, ..., 6$,[15,16] and CH_3SF and CH_3SSCH_2[17] as well as C_2H^-, $C_2H_3^-$, and $C_2H_5^-$.[18] In addition, we have applied the same method to determine the energies of the dissociation reactions involving CH_3S, CH_2SH, and their cations and anions,[19] $HSCH_2CH_2SH$,[20] and C_2H_3Cl and $C_2H_3Cl^+$.[21] In all instances, the calculated results are in good to excellent agreement with the experimental data. In fact, there are also cases we use the G2 results to suggest preferred values where

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TABLE 2: G2 Total Energies (E_0), Enthalpies (H_{298}), Standard Heats of Formation at 0 K(ΔH°_{f0}) and 298 K(ΔH°_{f298}) of Isomeric Cl_2O_2 and $Cl_2O_2^+$ and Their Fragments, and the Ionization Energies (IE) of Isomeric Cl_2O_2 and Their Neutral Fragments

species	E_0 (hartrees)	H_{298} (hartrees)[a]	ΔH°_{f0} (kJ mol^{-1})[a,b]	ΔH°_{f298} (kJ mol^{-1})[a,b]	IE (eV)[b]
ClOOCl	−1069.547 62	−1069.542 26	128.2 (136 ± 8[d])	125.7 (133 ± 8[d])	10.98 (11.05 ± 0.05[e])
$ClOOCl^+$	−1069.144 09	−1069.138 51	1187.7	1185.7 (1199 ± 12[e])	
$ClClO_2$	−1069.536 65	−1069.531 40	157.0	154.2	10.93
$ClClO_2^+$	−1069.135 04	−1069.128 73	1211.4	1211.4	
ClOClO	−1069.528 91	−1069.523 29	177.3	175.5	10.33
$ClOClO^+$	−1069.149 30	−1069.143 66	1174.0	1172.2	
ClClO	−994.463 80	−994.459 16	148.6 (71.30 ± ?[d])	148.0 (70 ± 30[d])	10.30
$ClClO^+$	−994.085 23	−994.080 65	1142.6	1141.8	
ClOCl	−994.490 99	−994.486 59	77.3 (82.81[d] ± ?[d,f])	76.0 (82.8 ± 2[d,f])	10.89 (10.94[f])
$ClOCl^+$	−994.090 78	−994.086 17	1128.0 (1138[f])	1127.3 (1136[f])	
ClOO	−609.826 09	−609.821 84	126.5 (91.66[d] ± ?[d])	125.5 (90 ± 5[d])	11.12
$ClOO^+$	−609.417 26	−609.413 05	1199.8	1198.8	
OClO	−609.829 34	−609.825 24	117.9 (99 ± ?[d,f])	116.6 (97 ± 8[d,f])	10.53 (10.36 ± 0.02,[f] 10.33 ± 0.02[g])
$OClO^+$	−609.442 20	−609.438 20	1134.4 (1099[f])	1132.8 (1097[f])	
ClO	−534.756 16	−534.752 76	110.4 (101.03 ± ?[d,f])	111.1 (101.63 ± 0.1[d,f])	10.76 (10.85 ± 0.05,[e] 10.95[f])
ClO^+	−534.360 66	−534.357 30	1148.8 (1158[f])	1149.4 (1158[f])	
Cl[c]	−459.676 63	−459.674 27			12.85 (12.97)
Cl^+ [c]	−459.204 54	−459.202 18			
O[c]	−74.982 03	−74.979 67			13.53 (13.61)
O^+ [c]	−74.484 97	−74.482 61			

[a] The way of obtaining H_{298}, ΔH°_{f0}, and ΔH°_{f298} from E_0 is described in detail in ref 17. [b] Experimental results, where available, are given in parentheses. [c] Reference 8. [d] Reference 2. [e] Reference 3. [f] Reference 23. [g] Flesh, R.; Rühl, E.; Hottmann, K.; Baumgärtel, H. *J. Phys. Chem.* **1993**, *97*, 837.

TABLE 3: G2 Dissociation Energies (D_0) for the Isomeric Cl_2O_2 and $Cl_2O_2^+$ [a]

reaction	D_0 (eV)
(a) $ClOOCl \rightarrow ClOO + Cl$	1.22
(b) $ClOOCl \rightarrow 2ClO$	0.96 (0.73 ± 0.08[b] at 298 K)
(c) $ClOOCl^+ \rightarrow ClOO^+ + Cl$	1.37
(d) $ClOOCl^+ \rightarrow ClOO + Cl^+$	3.09
(e) $ClOOCl^+ \rightarrow ClO^+ + ClO$	0.74 (0.53 ± 0.19[c] at 298 K)
(f) $ClClO_2 \rightarrow OClO + Cl$	0.83
(g) $ClClO_2 \rightarrow ClClO + O$	2.47
(h) $ClClO_2^+ \rightarrow OClO + Cl^+$	2.75
(i) $ClClO_2^+ \rightarrow OClO^+ + Cl$	0.44
(j) $ClClO_2^+ \rightarrow ClClO + O^+$	5.07
(k) $ClClO_2^+ \rightarrow ClClO^+ + O$	1.84
(l) $ClOClO \rightarrow ClOCl + O$	1.52
(m) $ClOClO \rightarrow OClO + Cl$	0.62 (0.59 ± 0.1[d])
(n) $ClOClO \rightarrow 2ClO$	0.45
(o) $ClOClO^+ \rightarrow ClOCl + O^+$	4.72
(p) $ClOClO^+ \rightarrow ClOCl^+ + O$	2.08
(q) $ClOClO^+ \rightarrow OClO + Cl^+$	3.14
(r) $ClOClO^+ \rightarrow OClO^+ + Cl$	0.83 (0.62 ± 0.1[d])
(s) $ClOClO^+ \rightarrow ClO + ClO^+$	0.88

[a] Calculated using E_0 values given in Table 2. Available experimental data are given in parentheses. [b] Reference 2. [c] Reference 3. [d] See text.

the experimental data are either not very accurate or in conflict with each other.[16] There are also examples where the G2 results are used to revise experimental data.[22]

Discussion

As can be seen from Table 2, there are three Cl_2O_2 isomers: ClOOCl (C_2 symmetry), $ClClO_2$ (C_s), and ClOClO (C_1). There are two isomers for Cl_2O: ClClO (C_s) and ClOCl (C_{2v}); there are also two ClO_2 isomers, ClOO (C_s) and OClO (C_{2v}). All these neutral species, along with their cations, as well as ClO and ClO^+, have been studied with the G2 procedure.

Ionization Energies. Comparing the G2 and experimental IE's for the neutral species listed in Table 2, it is seen that the two sets of data are in general in very good agreement with each other. The largest discrepancy occurs in the case of OClO, whose G2 and experimental IE's are 10.53 and 10.36 ± 0.02[23] eV, respectively. As mentioned in the previous section, the error range for G2 results is ±0.15 eV. So the two IE's for OClO may still be termed to be in agreement with each other.

In a recent study, Schwell and co-workers[3] measured the IE of a dimer of ClO using synchrotron radiation in combination with photoionization mass spectrometry. They found that the ionization threshold of $Cl_2O_2^+$ occurs at 11.5 ± 0.05 eV. In order to identify the Cl_2O_2 formed, they calculated the vertical IE's of ClOOCl, $ClClO_2$, and ClOClO using the Green's function method with various basis sets. Upon obtaining the vertical IE's, they then estimated the adiabatic IE's indirectly. By comparing the adiabatic IE's with the experimental measurement, they concluded that the dimer formed was ClOOCl. As can be seen from Table 2, the G2 IE's for ClOOCl and $ClClO_2$ are very similar, even though the ΔH°_f's of ClOOCl and $ClOOCl^+$ are different respectively from those of $ClClO_2$ and $ClClO_2^+$. Hence, it is not viable to identify the Cl_2O_2 formed by only comparing the measured and calculated IE's of isomers.

In the experiments of Schwell and co-workers,[3] Cl_2O_2 was formed by the dimerization of ClO. From the consideration of atomic connectivity, G2 thermal stability, and IE's of the isomers, it is reasonable to conclude that the dimer Cl_2O_2 formed was indeed ClOOCl.

Heats of Formation. Examining Table 2, it can be seen that most of the G2 ΔH°_f's are in good agreement with the experimentally determined data. Most importantly, the ΔH°_f's of ClOOCl and $ClOOCl^+$ are in excellent agreement with the observed data. This agreement should lend confidence to the G2 ΔH°_f's of $ClClO_2$ and ClOClO and their cations, for which experimental data are lacking. It is seen that the largest discrepancy between experimental and G2 ΔH°_f's occurs in the case of ClClO. However, since the error range for the experimental data (±30 kJ mol^{-1}) is so large, this measurement clearly deserves a reexamination.

Energies of Dissociation Reaction. The D_0 values of 19 dissociation reactions involving ClOOCl, $ClClO_2$, and ClOClO and their cations can be easily calculated using the G2 E_0's listed in Table 2. Examining the results summarized in Table 3, its is seen that experimental comparison can be made only for reactions b and e. In both instances, the experimental and

G2 D_0's may be termed to be in fair agreement with each other. Hence, the D_0's of the remaining 17 reactions can be viewed as reliable estimates.

Besides providing estimates for bond energies in various Cl_2O_2 isomers and their cations, the data in Table 3 can also be used to identify the isomers involved in aforementioned the ClO dimerization study by Schwell et al.[3] In addition to the formation of ClOOCl, as previously concluded, Schwell and co-workers also found an appearance energy (AE) for $OClO^+$ at 10.95 ± 0.1 eV. This value is higher than the IE of OClO (see Table 2), indicating that $OClO^+$ is not efficiently formed as a neutral species in the original cold flow system. Hence, these researchers concluded that $ClClO_2$ and/or ClOClO are/is also formed in the flow tube system. Since $OClO^+$ can be produced in the dissociative photoionization of either $ClClO_2$ or ClOClO, Schwell and co-workers could not conclude which isomer was formed.

If we associate the photoionization onset of $OClO^+$ with its thermochemical onset, $AE(OClO^+)$ is simply the energy of the reaction

$$\text{ClOClO or ClClO}_2 \xrightarrow{\text{AE(OClO}^+)} \text{OClO}^+ + \text{Cl} + \text{e}^- \qquad (1)$$

In the event ClOClO is indeed formed, it can be readily shown that

$$D_0(\text{OClO}^+{-}\text{Cl}) = \text{AE(OClO}^+) - \text{IE(ClOClO)} \qquad (2)$$

and

$$D_0(\text{OClO}{-}\text{Cl}) = \text{AE(OClO}^+) - \text{IE(OClO)} \qquad (3)$$

If we use the experimental IE(OClO) (10.36 ± 0.02 eV) and G2 IE(ClOClO) (10.33 eV) given in Table 2, we obtain

$$D_0(\text{OClO}^+{-}\text{Cl}) = 0.62 \pm 0.1 \text{ eV} \qquad (4)$$

and

$$D_0(\text{OClO}{-}\text{Cl}) = 0.59 \pm 0.1 \text{ eV} \qquad (5)$$

These two D_0's are in agreement with those calculated for reactions r and m (Table 3), respectively. Should we assume $ClClO_2$ is involved in process 1, similar calculations would lead to $D_0(O_2Cl{-}Cl)$ (0.59 ± 0.1 eV) and $D_0(O_2Cl^+{-}Cl)$ (0.02 ± 0.1 eV) values which are not in agreement with the energies for reactions f and i (Table 3). Hence, this analysis suggests that ClOClO is involved in the measurement of $AE(OClO^+)$. Recalling that the study of Schwell et al.[3] is the dimerization of ClO, it is not unreasonable to find that both ClOOCl (major product) and ClOClO (minor product) are formed.

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References and Notes

(1) Jensen, F.; Oddershede, J. *J. Phys. Chem.* **1990**, *94*, 2235.

(2) Abramowitz, S.; Chase, M. W., Jr. *Pure Appl. Chem.* **1991**, *63*, 1449.

(3) Schwell, M.; Jochims, H.-W.; Wasserman, B.; Rockland, U.; Flesch, R.; Rühl, E. *J. Phys. Chem*., in press.

(4) McGrath, M. P.; Clemitshaw, K. C.; Rowland, F. S.; Hehre, W. J. *J. Phys. Chem.* **1990**, *94*, 6126.

(5) Morris, V. R.; Bhatia, S. C.; Dibble, T. S.; Francisco, J. S. *J. Chem. Phys.* **1996**, *104*, 5345.

(6) Pak, Y.; Woods, R. C. *J. Chem. Phys*. **1996**, *104*, 5547.

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.: Gill, P. M. W.; Johnson, B. J.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrewski, V. G., Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision A1; Gaussian, Inc.: Pittsburgh, PA, 1995.

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

(9) Ma, Z.-X.; Liao, C.-L.; Yin, H.-M.; Ng, C. Y.; Chiu, S.-W; Ma, N. L.; Li, W.-K. *Chem. Phys Lett.* **1993**, *213*, 250.

(10) Ma, Z.-X; Liao, C. L.; Ng, C. Y.; Cheung, Y.-S.; Li, W.-K.; Baer, T. *J. Chem. Phys.* **1994**, *100*, 4870.

(11) Cheung, Y.-S.; Li, W.-K. *J. Mol. Struct. (THEOCHEM)* **1995**, *339*, 25.

(12) Cheung, Y.-S.; Li, W.-K. *Chem. Phys. Lett.* **1994**, *223*, 383.

(13) Cheung, Y.-S.; Li, W.-K. *J. Chem. Res., Synop.* **1994**, 352.

(14) Cheung, Y.-S.; Li, W.-K. *J. Mol. Struct. (THEOCHEM)* **1995**, *333*, 135.

(15) Cheung, Y.-S.; Li, W.-K.; Ng, C. Y. *J. Chem. Phys*. **1994**, *101*, 3412.

(16) Cheung, Y.-S.; Chen, Y.-J.; Ng, C. Y.; Chiu, S.-W.; Li, W.-K. *J. Am. Chem. Soc.* **1995**, *117*, 9725.

(17) Cheung, Y.-S.; Li, W.-K.; Ng, C.-Y. *J. Phys. Chem.* **1995**, *99*, 5967.

(18) Sou, W.-I.; Li, W.-K. *J. Chem. Res., Synop.* **1995**, 464.

(19) Chiu, S.-W.; Li, W.-K.; Tzeng, W.-B,; Ng, C.-Y. *J. Chem. Phys.* **1992**, *97*, 6557.

(20) Zhao, H.-Q.; Cheung, Y.-S.; Liao, C.-L.; Ng, C. Y.; Li, W.-K.; Chiu, S.-W. *J. Chem. Phys.* **1996**, *104*, 130.

(21) Sheng, L.; Qi, F.; Tao, L.; Zhang, Y.; Yu, S.; Wong, C.-K.; Li, W.-K. *Int. J. Mass Spectrom. Ion Processes* **1995**, *148*, 179.

(22) See, for example: Rusic, B.; Appleman, E.; Berkowitz, J. *J. Chem. Phys.* **1991**, *95*, 7957.

(23) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1).