Equilibrium Constants of the Reaction of Cl with O_2 in the Formation of ClOO[†]

Kohsuke Suma, Yoshihiro Sumiyoshi, and Yasuki Endo*

Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo,
Komaba, Meguro-ku, Tokyo 153-8902, Japan

Shinichi Enami, Simone Aloisio, Satoshi Hashimoto, and Masahiro Kawasaki

Department of Molecule Engineering and Graduate School of Global Environmental Studies,
Kyoto University, Kyoto 615-8510, Japan

Satoshi Nishida and Yutaka Matsumi

Solar-Terrestrial Environment Laboratory and Graduate School of Sciences, Nagoya University,
Toyokawa 442-8505, Japan

Received: February 27, 2004; In Final Form: May 19, 2004

The equilibrium constants for the formation of ClOO from Cl and O_2 are experimentally measured at 212−245 K using cavity ring-down spectroscopy. A van't Hoff plot analysis yields $\Delta H_r = 4.8 \pm 1.5$ kcal mol^{-1}. The Cl−OO bond dissociation energy is determined to be 4.69 ± 0.10 kcal mol^{-1} from the present and previously reported temperature dependences of the equilibrium constant by the third-law analysis utilizing our recent accurate rotational spectroscopic data. High level ab initio calculations using MRSDCI+Q with the complete basis set extrapolation are also performed. The present ab initio calculations yield the Cl−OO bond dissociation energy to be 4.56 kcal mol^{-1}.

Introduction

In the lower stratosphere, ClOO works as a short-lived intermediate in the catalytic ozone destruction cycle[1]

$$\mathrm{Cl} + \mathrm{O_2} + \mathrm{M} \leftrightarrow \mathrm{ClOO} + \mathrm{M} \qquad (1)$$

$$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2} \qquad (2)$$

$$\mathrm{ClO} + \mathrm{ClO} + \mathrm{M} \rightarrow \mathrm{ClOOCl} + \mathrm{M} \qquad (3)$$

$$\mathrm{ClOOCl} + h\nu \rightarrow \mathrm{ClOO} + \mathrm{Cl} \qquad (4)$$

ClOO is also involved in the reaction of BrO + ClO → Br + ClOO.[1,2] Thus, ClOO is considered to be a temporary sink for the Cl atoms in the polar stratosphere mainly due to the equilibrium reaction 1. Thermodynamic and kinetic studies for ClOO were reported by Baer et al.,[3] Mauldin et al.,[4] and Nicovich et al.,[5] where they determined the Cl−OO bond dissociation energy by the third-law analysis: $D_0 = 4.83 \pm 0.05$,[3] 4.6 ± 0.4,[4] and 4.76 ± 0.49[5] kcal mol^{-1}, respectively. These results indicate that the Cl−OO bond is as weak as the hydrogen bond. In kinetics experiments of this reaction, when the concentration of ClOO is high, the self-reaction becomes dominant:[3]

$$\mathrm{ClOO} + \mathrm{ClOO} \rightarrow \text{products} \qquad (5)$$

With a highly sensitive absorption spectroscopic method, e.g. cavity-ring down spectroscopy (CRDS), which allows us to perform the study under lower concentrations of ClOO, the rate of the self- reaction can be reduced to obtain the equilibrium constant for reaction 1 with higher accuracy.

To clarify the reported anomalously small Cl−OO bond dissociation energy and investigate its implications on the atmospheric chemistry, many theoretical studies have been reported.[6−15] However, their results deviate significantly depending on the calculation method. Since the structure of ClOO has recently been determined precisely from the rotational constants measured by FTMW and FTMW-mmW double resonance spectroscopy under cold molecular beam conditions,[16] it is now possible to estimate the thermodynamic parameters with a help of high level ab initio calculations. In the present work, we have performed experimental and theoretical studies on the thermodynamic property of the equilibrium reaction 1. CRDS is used to obtain experimental data. Theoretical calculations at the MRSDCI+Q level have been performed to obtain the potential energy surface and the bond dissociation energy, which is compared to the experimental results.

Experimental Section

CRDS has been widely applied to spectroscopic and chemical kinetic studies.[17−19] The CRDS apparatus used in the present study has been described elsewhere.[20−22] After the photolysis laser beam traverses a glass tube reactor nearly collinear to the axis of the ring-down cavity, the probe laser beam is injected through one of two high-reflectivity mirrors (Research Electro-Optics), which make up the ring-down cavity of 1.04 m. The probe laser beam is used to monitor the concentration of ClOO at 266 nm.[23] The length of the reaction region is 0.20 m. Light leaking from the outlet mirror is detected by a photomultiplier tube through a narrow band-pass filter. The decay of the light intensity is recorded using a digital oscilloscope and transferred to a personal computer.

---

* To whom correspondence should be addressed. Fax: +81-3-5454-6721. E-mail: endo@bunshi.c.u-tokyo.ac.jp.

[†] Part of the special issue "Richard Bersohn Memorial Issue".

10.1021/jp049124e CCC: $27.50

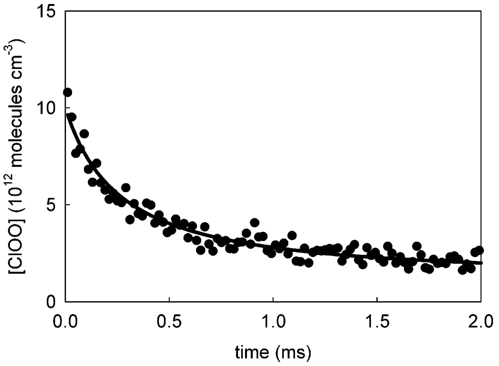

Figure 1. Typical decay profile of the ClOO radical monitored at 266 nm at $T = 217$ K and $P = 97$ Torr with N_2 diluent. $[Cl_2] = 5.1 \times 10^{15}$ molecules cm^{-3}; $[O_2] = 4.0 \times 10^{18}$ molecules cm^{-3}. The solid curve is the best-fit one for eq 7.

The reaction cell consists of a Pyrex glass tube (21 mm i.d.). The temperature of the gas flow region is controlled over the range 212−273 K. However, only very weak absorption of ClOO is observed above 245 K. The difference between the temperatures of the sample gas at the entrance and the exit of the gas flow region is <0.4 K. The total flow rate is about 1000 cm^3 min^{-1} (STP). The 355 nm output of a Nd^{3+}:YAG laser is used to dissociate Cl_2 to give the Cl atoms. The concentration of Cl_2 is typically 1×10^{15} molecules cm^{-3}. Time profiles of the ClOO concentration are measured between 5 μs and 10 ms after the initial photolysis laser pulses. A large excess amount of O_2, on the order of 10^{18}−10^{19} molecules cm^{-3}, is used to maintain the pseudo-first-order reaction conditions with a N_2 gas diluent.

To estimate the initial concentration of the Cl atoms, $[Cl]_0$, the loss of O_3 and the production of ClO at 273 K is measured by CRDS at 266 nm for the mixture of $Cl_2/O_3/O_2$ with photolysis of Cl_2 at 355 nm with $[Cl_2] = (1-10) \times 10^{15}$ molecules cm^{-3}:

$$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2} \tag{6}$$

At this temperature the formation of ClOO is negligible. O_3 is produced by irradiating an oxygen gas flow (>760 Torr) with a low-pressure Hg lamp (Hamamatsu Photonics) and its typical concentration is $>1 \times 10^{13}$ molecules cm^{-3}. Using the reported absorption cross section of ClO,[4] the initial concentration of the Cl atoms is estimated to be $[Cl]_0 = 7.2 \times 10^{12}$ molecules cm^{-3} at 273 K when $[Cl_2] = 2.8 \times 10^{15}$ molecules cm^{-3}. The contribution of the O_3 absorption at 266 nm is taken into account in the estimation. When the temperatures are lowered for the measurements of ClOO, the photolysis laser intensity is kept constant. For the estimation of the initial concentrations of the Cl atoms at different temperatures of 212−245 K, the temperature dependence in the Cl_2 absorption cross sections is taken into account.[2]

Results and Discussion

Cavity Ring-Down Spectroscopic Measurements. Figure 1 shows a typical decay profile of ClOO at 217 K and 71 Torr of the total pressure with $[Cl_2] = 5.1 \times 10^{15}$ and $[O_2] = 3.8 \times 10^{18}$ molecules cm^{-3}. The concentration of ClOO is depleted due mostly to the self- reaction. To rule out the reaction with chlorine, the reaction of ClOO + Cl_2 at 213 K and 125 Torr of the total pressure is tested. The concentrations of the Cl atoms are kept constant for the range $[Cl_2] = (3-20) \times 10^{15}$ molecules cm^{-3} by adjusting the photolysis laser intensity. No appreciable change in the cavity-ring down decay time is observed as a function of the Cl_2 concentration. Thus, ClOO does not react with Cl_2 under the present conditions. Including the effect of the diffusion of ClOO from the CRDS detection region, the decay of [ClOO] is analyzed as a sum of the first- and second-order kinetics by the following equation

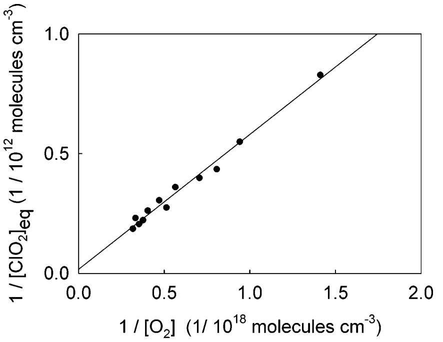

Figure 2. $[ClOO]_{eq}$ vs $[O_2]$ for eq 9. $T = 231$ K and $P = 86$ Torr with N_2 diluent. $[Cl_2] = 9.2 \times 10^{15}$ molecules cm^{-3}; $[O_2] = (3-12) \times 10^{18}$ molecules cm^{-3}

TABLE 1: Temperature Dependence of Equilibrium Constant K_P

T/K	K_p/bar^{-1}
212	2.7
217	4.0
222	1.9
226	3.2
231	0.89
235	1.5
245	0.70

$$\frac{1}{[\mathrm{ClOO}]_t} = \left\{\left(\frac{1}{[\mathrm{ClOO}]_0} + \frac{2k_5}{k^{\mathrm{diff}}}\right)\exp(k^{\mathrm{diff}}t) - \left(\frac{2k_5}{k^{\mathrm{diff}}}\right)\right\} \tag{7}$$

where $[ClOO]_t$ is the concentration of ClOO, $[ClOO]_0$ the initial concentration of ClOO, $k_5 = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [2], and k^{diff} is the diffusion constant. By fitting this equation to the decay curve of Figure 1, the absolute concentration $[ClOO]_0$ is obtained to be 1.1×10^{13} molecules cm^{-3}, where the reported absorption cross section of ClOO at 266 nm ($\sigma = 9.05 \times 10^{-18}$ cm^2 molecule^{-1}, see ref 4) is used. The equilibrium concentration, $[ClOO]_{eq}$, is approximated by this initial concentration $[ClOO]_0$ where the rise of the signal intensity is fast enough within the present time resolution of milliseconds.

The equilibrium constant of the ClOO formation reaction is determined by

$$K_C = [\mathrm{ClOO}]_{eq}/[\mathrm{Cl}]_{eq}[\mathrm{O_2}] \tag{8}$$

$$1/[\mathrm{ClOO}]_{eq} = 1/(K_C[\mathrm{O_2}][\mathrm{Cl}]_0) + 1/[\mathrm{Cl}]_0 \tag{9}$$

$$K_P = K_C/RT \tag{10}$$

From the slope of the plots of $1/[ClOO]_{eq}$ vs $1/[O_2]$, K_C is determined directly for the pressure range 15−80 Torr of O_2 with eq 9 as shown in Figure 2. No pressure dependence of the diluent N_2 gas on K_P is observed for the pressure range 20−70 Torr. Table 1 shows K_P thus determined for 212−245 K. Although the calculated enthalpy change depends on the temperature, it is small compared to the experimental errors of K_P, which are estimated to be less than 13%. Hence, we have experimentally determined ΔH_r and ΔS_r from the van't Hoff analysis:

$$\ln K_P = \Delta S/R - \Delta H_r/RT \tag{11}$$

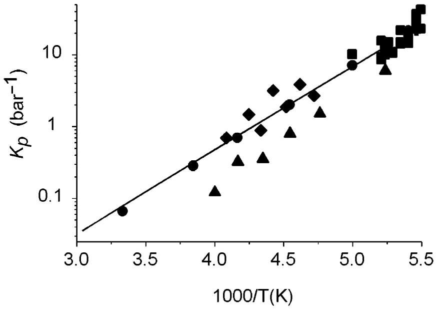

Figure 3. van't Hoff plots for K_P. Diamonds stand for the present results, circles for Baer et al.,[3] squares for Nicovich et al.,[5] and triangles for Mauldin et al.[4] The calculated K_P using the recommended value is also shown with a solid line.

Figure 3 gives $\Delta S_r = -20.0 \pm 7.0$ cal mol^{-1} K^{-1} and $\Delta H_r = -4.8 \pm 1.6$ kcal mol^{-1}, where the experimental errors of K_P at corresponding temperatures are also included.

Ab Initio Calculations. Ab initio calculations have been carried out using the MOLPRO 2002.6 suite of programs.[24] Since it is indispensable to take into account both the dynamic and static electron correlations and results deviate significantly depending on the method employed,[16] the calculations have been performed using the MRSDCI method including the Davidson correction with Dunning's correlation-consistent basis sets with diffuse orbitals (aug-cc-pVxZ; x = 2, 3, 4, 5).[25] A CASSCF calculation is carried out by distributing 13 electrons into 9 valence orbitals to obtain reference configurations for the subsequent MRSDCI calculation, where the 9 valence orbitals correspond to the atomic 2p and 3p orbitals of oxygen and chlorine, respectively. The subsequent MRSDCI calculation includes all single and double excitations from the three lowest valence orbitals not included in the CAS space, as well as those from the CASSCF determinant. This level of calculation is denoted as "MRSDCI(valence)" below. Although no significant change for the results has been observed by extending the CAS space, it was found that includion of the lowest three valence orbitals for the electron correlation has a large contribution to the binding energy. Thus, we have also performed MRSDCI calculations with additional excitations from the three more inner core 2p orbitals of the Cl atom, denoted as "MRSDCI (valence +3)".

Comparison with Previous Experiments. The present data are plotted in Figure 3 along with those of the previous studies for comparison purpose. Our values of K_P at several temperatures agree with those of Baer et al.[3] but are larger than those of Mauldin et al.[4] The absolute K_P values may have an error due to difficulties in the measurements of the absolute concentrations of the Cl atoms. The concentrations of Cl and ClOO in our case are lower than those of Mauldin et al. and Baer et al. by 1 and 4 orders of magnitude, respectively. The experimental condition by Baer et al. resulted in fast ClOO signal decays within 50 μs because of the high concentration of ClOO.[3] Since it becomes difficult to determine K_P at higher temperatures because of the low concentration of ClOO, the values of Mauldin et al. at the high temperature limit could have large error bars. To clarify this point, the present and the previously reported experimental values for K_P have been reanalyzed by the third-law analysis, where the partition function of ClOO is calculated using the recently reported rotational constants determined by FTMW and FTMW-mmW double resonance spectroscopy, A = 74541.9899 MHz, B = 4936.72861 MHz, C = 4621.1740 MHz,[16] and the vibrational frequencies by an IR experiment in an Ar matrix: $\nu_1 = 214.9$ cm^{-1}, $\nu_2 = 1477.8$ cm^{-1}, and $\nu_3 = 432.4$ cm^{-1}.[26] Although the previous studies in refs 3−5 also employed the third-law analysis, quite different molecular constants had been assumed for ClOO. The rotational constants are different from those determined by the FTMW experiment about 10−30%, and the assumed vibrational frequencies are also quite different due to a misassignment in the referenced paper.[27] The Cl−OO bond dissociation energies, D_0, determined by the present analysis from all the K_P values so far obtained are plotted in Figure 4. Our experimental results agree well with those of Baer et al.[3] and Nicovich et al.[5] Those of Mauldin et al.[4] are smaller than others and depend on the temperature. Thus, a recommended value of D_0 is determined to be 4.69 ± 0.10 kcal mol^{-1} by averaging our data and those from refs 3 and 5, which is shown in Figure 4 with a straight line, where a relatively small error can be given because a large number of experimental data are taken into account including those previously obtained for the determination of D_0. The equilibrium constant K_P calculated by this recommended value is also shown in Figure 3 with a solid line, and is approximated by

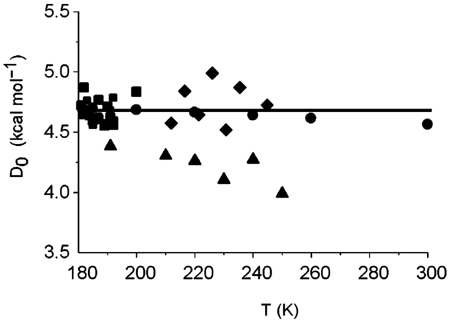

Figure 4. Cl−OO bond dissociation energy, D_0, determined by the third law analysis for experimental values of K_P. Diamonds stand for the present results, circles for Baer et al.,[3] squares for Nicovich et al.,[5] and triangles for Mauldin et al.[4] The recommended value is also shown with a straight line.

$$K_P = (1.04 \pm 0.04) \times 10^{-5} \times \exp((-2668 \pm 25)/T), \quad \text{for } T = 190-270 \text{ K} \tag{12}$$

Comparison of Experiment and ab Initio Calculation. One of the most reliable ab initio calculations reported so far is the one by Peterson et al.[6] with the MRSDCI method. Their results well reproduce some of the experimental results, such as the vibrational frequencies and the molecular structure. However, their Cl−OO bond dissociation energy, D_e = 2.46 kcal mol^{-1}, is much smaller than that obtained by correcting the zero point energy to the recommended value. Thus, although the global feature of the potential energy surface is well reproduced, the depth of the potential has not been reproduced well. This is mainly due to the fact that their calculations did not include excitations from the valence 2s and 3s orbital of the O and Cl atoms, respectively, for the MRSDCI calculations. A much larger MRSDCI(valence)/aug-cc-pVQZ level of calculation, which includes these correlations, yields 4.33 kcal mol^{-1} for D_e. Since the calculation do not show saturation against the size of the basis sets even for aug-cc-pV5Z, the discrepancy of the theoretical value of D_e in ref 13 is also ascribed to the limited size of the basis sets. Thus, the CBS extrapolation is employed to estimate D_e in the present study. Results of different basis sets are fitted to eq 13.[28]

$$D_e(x) = D_e^{\text{CBS}} + a e^{-bx} \tag{13}$$

where x is the index of the basis set (aug-cc-pVxZ, x = 2,3,4,5) and a and b are constants which are independent of the sizes on basis sets. Thus, D_e^{CBS} is calculated to be 5.15 kcal mol^{-1}, which corresponds to $D_0 = 4.33$ kcal mol^{-1} and agrees with the experimental value, $D_0 = 4.69$ kcal mol^{-1}. It is expected that the bond dissociation energy becomes larger by adding more inner core electron correlations. Thus, we have also performed a MRSDCI calculation including the correlation of the inner core 2p orbitals of the Cl atom (MRSDCI (valence +3)). D_0^{CBS} is calculated to be 4.65 kcal mol^{-1}. This fact indicates the dynamic electron correlation is still insufficient for the ab initio calculation of ClOO, and inclusion of more inner core electron correlations is expected to reduce the discrepancy. However, the spin−orbit interaction has not been taken into account. The spin−orbit interaction lowers D_e about 1 kcal mol^{-1} so that the discrepancy becomes larger.

Conclusion

Using an advent of the high sensitivity of cavity ring-down spectroscopy, we have determined the temperature-dependent equilibrium constant for the formation of ClOO from the reaction of Cl with O_2. The third-law analysis is applied to these data obtained and previously reported values, taking into account the temperature dependence of the K_P, using the recently determined experimental molecular constants. The Cl−OO bond dissociation energy, D_0, is determined to be 4.69 ± 0.10 kcal mol^{-1}, yielding a temperature-dependent equilibrium constant of

$$K_P = (1.04 \pm 0.04) \times 10^{-5} \times \exp((-2668 \pm 25)/T), \quad \text{for } T = 190-270 \text{ K}$$

A reasonable agreement between the theoretically derived D_0 and that determined by the experiments are obtained. It is found that both the dynamic and static electron correlations are indispensable for the ab initio calculations of ClOO. In particular, the excitations from the inner core orbitals are important to properly describe the weak Cl−OO bond.

Acknowledgment. This work is supported by a Grant-in-Aid for the priority research field “Radical Chain Reactions” (13127101 and 13127103) and a Grant-in-Aid by Ministry of Education, Culture, Sports, Science, and Technology (07454148). We thank Junya Ueda and Yuki Ito of Kyoto University for their help in experiments.

References and Notes

(1) Finlayson-Pitts, B. J.; Pitts, J. N. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications*; Academic Press: San Diego, CA, 2000.

(2) 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 Stratospheric Modeling: Evaluation 14*; Jet Propulsion Laboratory: Pasadena, CA, 2003.

(3) Baer, S.; Hippler, H.; Rahn, R.; Siefke, M.; Seitzinger, N.; Troe, J. *J. Chem. Phys.* **1991**, *95*, 6463.

(4) Mauldin, R. L.; Burkholder, J. B.; Ravishankara, A. R. *J. Phys. Chem.* **1992**, *96*, 2582.

(5) Nicovich, J. M.; Kreutter, K. D.; Shackelford, C. J.; Wine, P. J. *Chem. Phys. Lett.* **1991**, *179*, 367.

(6) Peterson, K. A.; Werner, H.-J. *J. Chem. Phys.* **1992**, *96*, 8948.

(7) Francisco, J. S.; Sander, S. P. *J. Chem. Phys.* **1993**, *99*, 2897.

(8) Jafri, J. A.; Lengsfield, B. H., III; Phillips, D. H. *J. Chem. Phys.* **1985**, *83*, 1693.

(9) Fernández, B.; Christiansen, O.; Jørgensen, P.; Byberg, J.; Gauss, J.; Ruud, K. *J. Chem. Phys.* **1997**, *106*, 1847.

(10) Craven, W.; Knowles, D. B.; Murrell, J. N.; Vincent, M. A.; Watts, J. D. *Chem. Phys. Lett.* **1985**, *116*, 119.

(11) Alcami, M.; Mo, O.; Yanez, M.; Cooper, IL. *J. Chem. Phys.* **2000**, *112*, 6131.

(12) Beltran, A.; Andres, J.; Noury, S.; Silvi, B. *J. Phys. Chem.* **1999**, *103*, 3078.

(13) Michael, F.; Dieter, C. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2320.

(14) Li, Q.-S.; Lue, S. F.; Xu, W. G.; Xie, Y. M.; Schaefer, H. F., III. *J. Phys. Chem. A.* **2002**, *106*, 12324.

(15) Zhu, R. S.; Lin, M. C. *J. Chem. Phys.* **2003**, *119*, 2075.

(16) Suma, K.; Sumiyoshi, Y.; Endo, Y. To be published in *J. Chem. Phys.*

(17) O’Keefe, A.; Deacon, D. A. G. *Rev. Sci. Instrum.* **1988**, *59*, 2544.

(18) Yu, T.; Lin, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 4371.

(19) Wheeler, M. D.; Newman, S. M.; Orr-Ewing, A. J.; Ashfold, M. N. R. *J. Chem. Soc., Faraday. Trans.* **1998**, *94*, 337.

(20) Nakano, Y.; Enami, S.; Nakamichi, S.; Aloisio, S.; Hashimoto, S.; Kawasaki, M. *J. Phys. Chem. A.* **2003**, *107*, 6381.

(21) Enami, S.; Nakano, Y.; Hashimoto, S.; Aloisio, S.; Kawasaki, M.; Francisco. J. S. *J. Phys. Chem. A.*, published on line June 8, 2004, http://dx.doi.org/10.1021/jp049772y.

(22) Enami, S.; Junya, U.; Goto, M.; Nakano, Y.; Aloisio, S.; Hashimoto, S.; Kawasaki, M. *J. Phys. Chem. A.*, in press.

(23) Johnston, H. S.; Morris, E. D.; Van den Bogaerde, J. *J. Am. Chem. Soc.* **1969**, *91*, 7712.

(24) MOLPRO is a package of ab initio programs designed by: Werner, H.-J.; Knowles, P. J. The authors are: 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.

(25) Kendall, R. A.; Dunning, T. H.. Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(26) Müller, H. S. P.; Willner, H. *J. Phys. Chem.* **1993**, *97*, 10589.

(27) Arkell, A.; Schwager, I. *J. Am. Chem. Soc.* **1967**, *89*, 5999.

(28) Peterson, K. A.; Kendall, R. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 1930.