

# Ab Initio Studies of ClO<sub>x</sub> Radical Reactions: V. Evidence for a New Path in the Cl + ClOOCl Reaction

R. S. Zhu and M. C. Lin\*

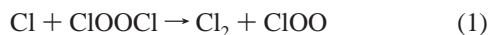
Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received: August 15, 2002; In Final Form: February 12, 2003

The mechanism for the reaction Cl + ClOOCl has been investigated by ab initio molecular orbital and transition-state theory calculations. The result shows that the reaction can produce both Cl<sub>2</sub> + ClOO and Cl<sub>2</sub>O + ClO. The former product pair can be formed by direct and indirect abstraction paths. The direct abstraction path, which dominates at low temperatures, takes place barrierlessly with the rate constant  $k_1 = 1.53 \times 10^{-13} T^{1.1} \exp(118/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in the temperature range of 200–1000 K. The rate constant of the indirect path, which occurs via the two isomers of the Cl–O(Cl)OCl complex lying 3 kcal/mol below the reactants,  $k_1' = 7.14 \times 10^{-12} T^{0.86} \exp(-2370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , accounting for less than 0.1% of the Cl<sub>2</sub> yield at 298 K but increasing to about 46% at 1000 K. The new Cl<sub>2</sub>O + ClO products can be produced by the fragmentation of the two complexes; the rate constant for their formation was found to be pressure-independent and can be expressed by  $k_2 = 2.19 \times 10^{-14} T^{0.70} \exp(-1110/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  covering the temperature range of 200–1000 K. Above room temperature, Cl<sub>2</sub>O formation becomes competitive; for example, its branching ratios,  $k_2/k_1$ , are predicted to be 0.19, 0.55, and 0.62 at 298, 500, and 1000 K, respectively. The predicted total rate constant agrees closely with available experimental results. The heat of formation of ClOOCl has been examined in detail using different reactions and computational methods. The results of these calculations converge to  $\Delta_f H^\circ_0(\text{ClOOCl}) = 30 \pm 2 \text{ kcal/mol}$ .

## I. Introduction

Chlorine peroxide (ClOOCl), formed by the recombination of ClO radicals, plays a pivotal role in the O<sub>3</sub>-destruction chemistry.<sup>1–3</sup> Its photodissociation reaction in the stratosphere regenerates Cl atoms and, to some extent, ClO radicals depending on the wavelength.<sup>4–9</sup> The reaction of ClOOCl with Cl is known to be very fast with the production of Cl<sub>2</sub> and ClOO exclusively,<sup>10,11</sup>



In principle, another exothermic product pair, Cl<sub>2</sub>O + ClO, could be formed and possibly quite competitively because two stable molecular complexes between Cl and ClOOCl were found to exist in our recent study of the reaction (vide infra). The formation of the complex might help promote the following reaction:



The objective of this study is to predict the relative contribution of the two product channels on the basis of ab initio molecular orbital and statistical rate constant calculations, which have been shown to be quite useful in estimating total rate constants and product branching ratios as well for several complex ClO<sub>x</sub> reactions in this laboratory.<sup>12–15</sup>

## II. Computational Methods

The geometries of the reactants, intermediates, transition states, and products of the Cl + ClOOCl reaction are computed

\* To whom correspondence should be addressed. E-mail address: chemmcl@emory.edu. National Science Council Distinguished Visiting Professor at Chiaotong University, Hsinchu, Taiwan.

at the G96LYP/6-311+G(3df) level with Barone and Adamo's Becke-type one-parameter functional using Gill96 exchange and LYP correlation.<sup>16</sup> Vibrational frequencies employed to characterize stationary points and zero-point energy (ZPE) corrections have also been calculated at this level of theory and have been used for the rate constant calculations. Intrinsic reaction coordinate (IRC) calculations<sup>17</sup> have been performed to confirm the connection of each transition state with designated reactants and products.

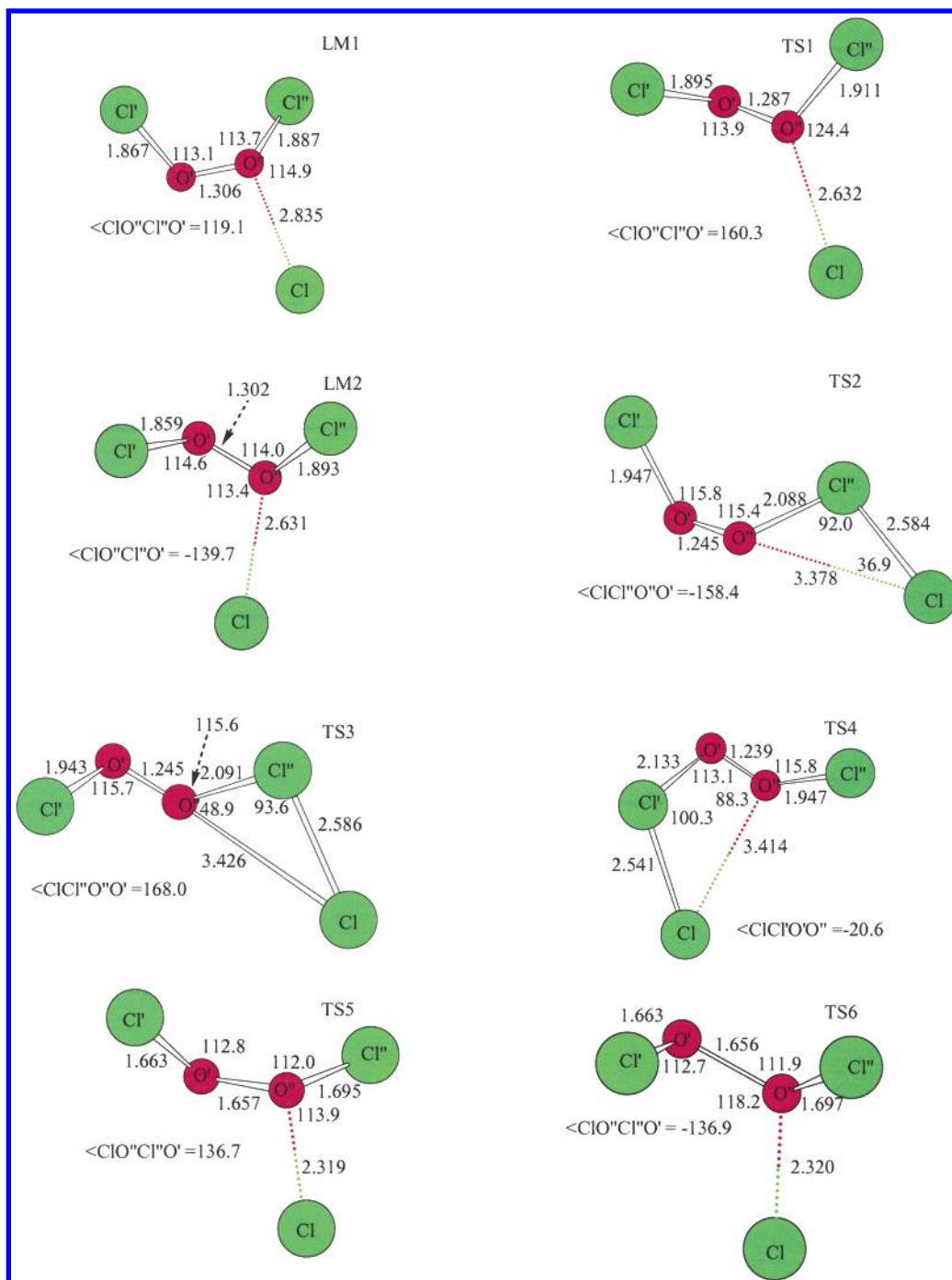
The energies of all species were calculated by the G2M method,<sup>18</sup> which uses a series of calculations with G96LYP/6-311+G(3df)-optimized geometries to approximate the CCSD-(T)/6-311+G(3df) level of theory, including a "higher level correction (HLC)" based on the number of paired and unpaired electrons. All calculations were carried out with Gaussian 98.<sup>19</sup>

The rate constants were computed with a microcanonical variational Rice–Ramsperger–Kassel–Marcus (RRKM) approach using the Variflex<sup>20</sup> and ChemRate codes.<sup>21</sup>

## III. Results and Discussion

### A. Potential Energy Surface and Reaction Mechanism.

For this reaction, the products are mainly produced via a doublet potential energy surface (PES). From the PES characteristics of the <sup>3</sup>O + OClO system,<sup>14</sup> we have learned that the transition states on this type of doublet PES are sensitive to the methods employed. To obtain reliable transition states, we first optimized one transition state (TS5 in Figure 1) structure at the G96LYP/6-311+G(3df), PW91PW91/6-311+G(3df), MPW1PW91/6-311+G(3df), B3LYP/6-311+G(3df), and MP2/6-311+G(2d) levels of theory. The  $\langle S^2 \rangle$  values determined by these methods are, correspondingly, 0.758, 0.760, 0.872, 0.847, and 1.565. The G2M barriers relative to the reactants based on these optimized



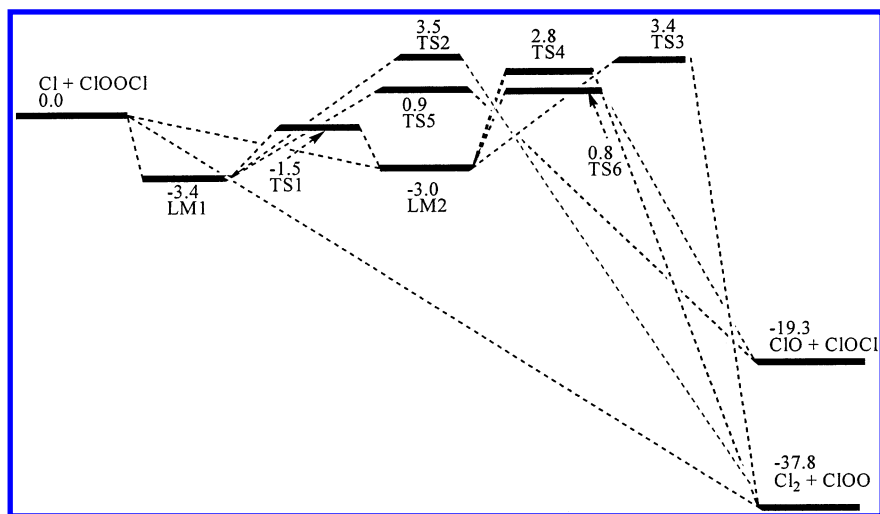
**Figure 1.** The optimized geometry of intermediates and transition states computed at the G96LYP/6-311+G(3df) level for the Cl + ClOOCl reaction.

structures are 0.86, 1.71, 14.3, 14.6, and 8.4 kcal/mol, respectively. From our previous calculation,<sup>14</sup> we noted that when an optimized molecular structure has a large  $\langle S^2 \rangle$  value, it is difficult to obtain a reliable G2M energy; therefore, the MPW1PW91/6-311+G(3df), B3LYP/6-311+G(3df), and MP2/6-311+G(2d) methods, which gave greater  $\langle S^2 \rangle$  values, were not used and only the G96LYP/6-311+G(3df) method was employed to optimize all other transition states or stable species for this reaction. However, we should note that the G2M(cc2)//PW91PW91/6-311+G(3df) method does give reasonable heat of formation for the ClOOCl molecule,  $33.9 \pm 0.9$  and  $31.7 \pm 0.7$  kcal/mol based on the reactions  $\text{Cl} + \text{ClOOCl} \rightarrow \text{ClO} + \text{ClOCl}$  and  $\text{Cl} + \text{ClOOCl} \rightarrow \text{Cl}_2 + \text{ClO}$ , respectively. These results are close to the experimental values, 29.7<sup>22</sup> and 32.6<sup>11</sup> kcal/mol and to our previously predicted value, 29.4 kcal/mol.<sup>14b</sup>

The PES and the heat of formation for ClOOCl predicted at the G2M(cc2)//G96LYP/6-311+G(3df) level of theory will be discussed below.

The optimized geometries of the intermediates and transition states for the reaction of Cl + ClOOCl are shown in Figure 1. The potential energy diagram obtained at the G2M//G96LYP/6-311+G(3df) level is presented in Figure 2. The vibrational frequencies and rotational constants are summarized in Table 1.

**Formation of Cl<sub>2</sub> + ClOO Products.** As discussed previously,<sup>14b</sup> among the five isomers of Cl<sub>2</sub>O<sub>2</sub>, the ClOOCl molecule with C<sub>2</sub> symmetry is most stable. Experimentally,<sup>10,11</sup> the Cl<sub>2</sub>-formation channel was found to be fast and has been assumed to be the only channel for the reaction. However, no detailed discussion on the mechanism has been presented in the literature.



**Figure 2.** The schematic energy diagram for the Cl–ClOOCl system computed at the G2M level.

**TABLE 1: Vibrational Frequencies and Rotational Constants of the Reactants, Intermediates, and Transition States for the Reaction Cl + ClOOCl Calculated at the G96LYP/6-311+G(3df) Level**

species	$B$ (GHz)	frequencies (cm <sup>-1</sup> )
ClOOCl	12.5, 2.0, 1.8	106, 256, 348, 515, 526, 1035
LM1	2.5, 1.1, 0.8	29, 41, 53, 107, 251, 366, 489, 538, 919
LM2	1.9, 1.6, 1.0	46, 57, 79, 112, 263, 362, 485, 542, 919
TS1	2.1, 1.2, 0.8	91i, 42, 67, 117, 227, 350, 489, 521, 971
TS2	7.1, 0.7, 0.7	70i, 37, 83, 178, 226, 314, 429, 529, 1182
TS3	5.0, 0.8, 0.8	83i, 20, 94, 185, 219, 318, 424, 531, 1180
TS4	3.0, 1.2, 1.0	139i, 41, 90, 186, 237, 319, 377, 530, 1209
TS5	2.5, 1.5, 1.0	222i, 45, 92, 119, 190, 268, 398, 602, 711
TS6	2.5, 1.5, 1.0	225i, 45, 93, 119, 189, 269, 389, 602, 710

As shown in Figure 2, several reaction paths can lead to the abstraction products, Cl<sub>2</sub> + ClOO.

**Direct Path.** In ClOOCl, the two O and the two Cl atoms are equivalent. In principle, Cl atom can attack one of the Cl or O in ClOOCl to form different products. Our ab initio results show that when the Cl atom attacks one of the Cl in ClOOCl, it directly leads to Cl<sub>2</sub> + ClOO barrierlessly with the exothermicity of 37.8 kcal/mol at the G2M level.

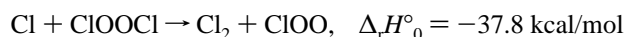
**Indirect Path.** As shown in Figures 1 and 2, the attacking Cl atom can form two isomeric complexes (LM1 and LM2) with ClOOCl, which will be labeled as Cl'O'O''Cl'' for the convenience of discussion. The two complexes have similar structural parameters (see Figure 1) except that their ClO''Cl'O' dihedrals, 119.1° and -139.7°, indicate that Cl attacks the O'' atom from different directions. They lie below the reactants by 3.4 and 3.0 kcal/mol at the G2M level. LM1 can readily isomerize to LM2 via TS1 with a 1.9 kcal/mol barrier.

LM1, having the O''–Cl bond length of 2.835 Å, is looser and can readily rotate; the interaction of Cl with Cl'' via TS2 can produce Cl<sub>2</sub> + ClOO (ClCl'' + Cl'O'O'') with a barrier above the reactants by 3.5 kcal/mol. In LM2, besides the possible interaction of Cl with Cl'' to eliminate ClCl'' via TS3 (with a barrier above the reactants by 3.4 kcal/mol), the Cl atom can also interact with Cl' to form ClCl' + Cl'O''O' via TS4 with a barrier above the reactants by 2.8 kcal/mol (see Figures 1 and 2).

**Formation of ClOCl + ClO Products.** As discussed in the above section, the reaction of Cl with ClOOCl can form two complexes, LM1 and LM2, which can not only undergo elimination of ClCl'' or ClCl' but also dissociate to give ClO''Cl'' + Cl'O' via the corresponding transition states TS5 and TS6. Similar to those of LM1 and LM2, the apparent difference in

structural parameters of TS5 and TS6 lies in the ClO''Cl'O' dihedrals, 136.7° and -136.9°, respectively. The breaking O'O'' bonds lengthen by about 0.35 Å in TS5 and TS6 compared with those in LM1 and LM2; the forming Cl–O'' bond lengths decrease from 2.835 and 2.631 Å in LM1 and LM2 to 2.319 and 2.320 Å in TS5 and TS6, respectively. At the G2M level, TS5 and TS6 lie above the reactants by 0.86 and 0.79 kcal/mol, respectively.

**Heat of Formation for ClOOCl.** Although the heat of formation of ClOOCl does not affect the predicted rate constants in the present case, because of its significant relevance to the stratospheric O<sub>3</sub>-destruction chemistry, we have examined the heat of formation of ClOOCl in greater detail. Based on the experimental heats of formation<sup>23</sup> for Cl, ClO, ClOCl, and ClOO and the predicted enthalpy changes for the two reactions



the heat of formation of ClOOCl was found to be 34.3 ± 0.5 and 32.9 ± 0.7 kcal/mol, respectively. The predicted values are consistent with the experimental values, 29.7<sup>22</sup> and 32.1 kcal/mol,<sup>11</sup> and are close to some of the previous theoretical estimates, 34.2<sup>24</sup> and 32.6<sup>25</sup> at the CCSD(T)/[65321/54321]//CCSD/TZ2P and MP2/6-31++(3d,2p) levels, which are somewhat larger than the predicted values, 29.4<sup>14b</sup> and 30.6,<sup>26</sup> calculated at the G2M//B3LYP/6-311+G(3df,2p) and G2 levels, respectively. Similarly, the predicted heats of reaction given above are also close to the corresponding experimental values, -16.8 and -36.9 kcal/mol. Apparently, for this system, the G2M//G96LYP/6-311+G(3df) method provides not only reasonable transition-state structures but also reliable energies compared with the G2M//PW91PW91/6-311+G(3df) and other methods as mentioned in the previous section.

Because of the apparent deviation of ~3 kcal/mol in the heat of formation of ClOOCl mentioned above, we have carried out additional calculations using several isodesmic reactions and computational methods as listed in Table 2. The results of these calculations converge to  $\Delta_f H^\circ_0 = 30$  kcal/mol with about ±2 kcal/mol deviation. This lower value in fact agrees more closely with the predicted dissociation energy of ClOOCl to 2ClO, 29.4 kcal/mol,<sup>14b</sup> which gave rise to a quantitative pressure-dependence prediction for the reverse association process measured experimentally as discussed in detail in ref 14b.

**B. Rate Constant Calculations.** The rate constant for the direct abstraction channel ( $k_1$ ) was calculated with the VARI-

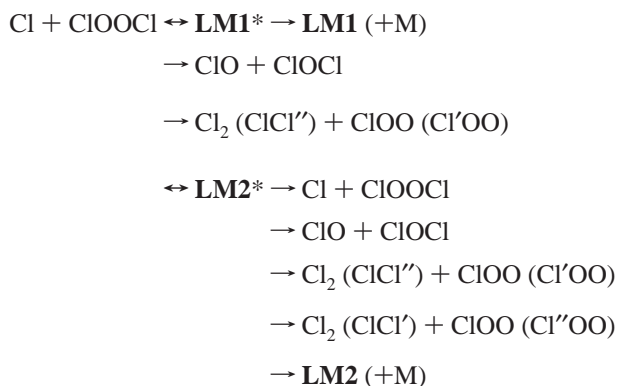
**TABLE 2: Comparison of the Predicted Heats of Formation (kcal/mol) for ClOOC1 at 0 K Based on Different Reactions and Methods with Available Data**

reaction	$\Delta_f H^\circ_0$
(1) ClO + ClO = ClOOC1	29.4 <sup>14b</sup>
(2) Cl + ClOOC1 = Cl <sub>2</sub> + ClOO	32.9 ± 0.7 <sup>a</sup> , 26.1 <sup>b</sup> , 33.6 <sup>c</sup> , 31.7 ± 0.7 <sup>d</sup>
(3) Cl + ClOOC1 = ClOCl + ClO	34.3 ± 0.5 <sup>a</sup> , 29.9 ± 0.5 <sup>b</sup> , 29.6 ± 0.5 <sup>c</sup> , 33.9 ± 0.5 <sup>d</sup>
(4) HO + ClOOC1 = HOOC1 + ClO <sup>e</sup>	29.3 ± 0.5 <sup>b</sup>
(5) HO <sub>2</sub> + ClOOC1 = HOOC1 + ClOO <sup>e</sup>	28.2 ± 1.5 <sup>b</sup>
(6) H + ClOOC1 = HOOC1 + Cl <sup>e</sup>	31.4 <sup>b</sup>
(7) HOOC1 + HCl = H <sub>2</sub> + ClOOC1 <sup>e</sup>	30.7 <sup>b</sup>
(8) HOOC1 + HOCl = H <sub>2</sub> O + ClOOC1 <sup>e</sup>	31.9 <sup>b</sup>
(9) HOOH + Cl <sub>2</sub> = H <sub>2</sub> + ClOOC1	28.3 <sup>b</sup>
(10) ClOOC1 + H <sub>2</sub> O = ClOCl + HOOH	32.1 ± 0.5, <sup>b</sup> 32.6 ± 3.2, <sup>25</sup> 34.2, <sup>24 f</sup> 30.6, <sup>26</sup> 29.7, <sup>22</sup> 32.1 <sup>11</sup>

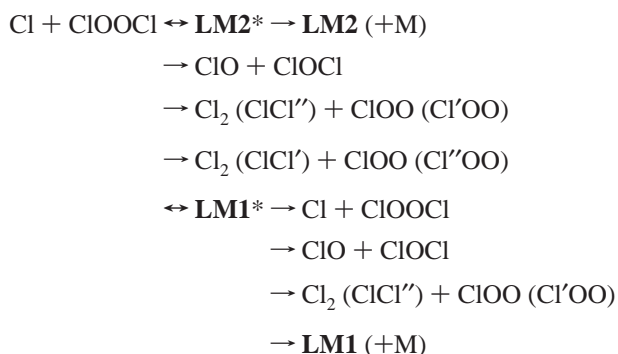
<sup>a</sup> G2M//G96/6-311+G(3df), this work. <sup>b</sup> G2M//B3LYP/6-311+G(3df), this work. <sup>c</sup> G96/6-311+G(3df), this work. <sup>d</sup> G2M//PW91PW91/6-311+G(3df), this work. <sup>e</sup> The heat of formation of HOOC1, 0.78 ± 0.5 kcal/mol, used in the reactions 4–8, is based on the reaction of HOOH + HOCl = HOOC1 + H<sub>2</sub>O at the G2M(CC2)//B3LYP/6-311+G(3df,2p) level; the heats of formation of other species are taken from ref 23. <sup>f</sup> This value becomes 32.6 ± 1 kcal/mol if the most recent heat of formation for Cl<sub>2</sub>O was used, as discussed in ref 14b.

FLEX code,<sup>20</sup> whereas those for the indirect association/disproportionation reactions were computed with the ChemRate code<sup>21</sup> coupling all intermediates involved in the forward and reverse reactions as shown below:

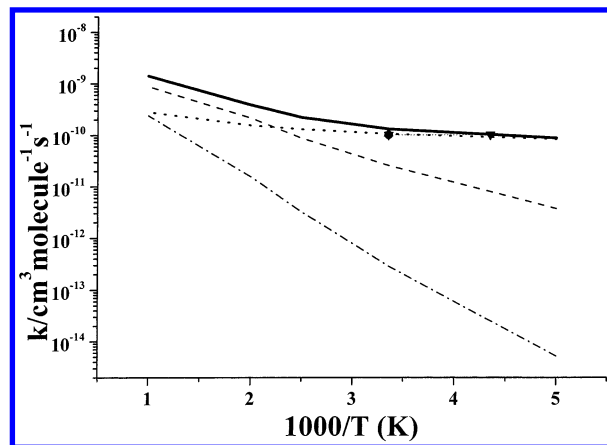
## Scheme 1



## Scheme 2



where \* denotes the chemically activated **LM1** or **LM2**. The energies plotted in Figure 2 and the vibrational frequencies and rotational constants listed in Table 1 were used in the calculation. Because the product formation processes were found to be pressure-independent, the Lennard-Jones (L-J) parameters re-



**Figure 3.** Comparison of the predicted rate constants with the experimental values in N<sub>2</sub>. Dotted and dashed-dotted lines represent the predicted formation rate constants of Cl<sub>2</sub> + ClOO,  $k_1$  and  $k_1'$ , respectively. Dashed line represents  $k_2$  for ClO + ClOCl formation, and the thick solid line represents the total rate constant. Symbols are experimental data of ref 11.

quired for the stabilization of ClO(Cl)OC1 (**LM1** and **LM2**) were assumed to be approximately the same as that of ClOOC1.<sup>14b</sup>

**Cl<sub>2</sub> + ClOO Formation.** As alluded to in the preceding discussion on the results of ab initio calculations, Cl<sub>2</sub> + ClOO can be directly and indirectly formed. The initial association process does not have a well-defined transition state because of the absence of an intrinsic reaction barrier. In this case, the Cl'O'O''Cl''-Cl complex on the Cl<sub>2</sub> + ClOO side was first located, and then the Cl-Cl'' bond length of this complex was varied from 2.037 to 4.637 Å, while other geometric parameters were fully optimized and their frequencies calculated at the G96LYP/6-311+G(3df) level. A smooth PES was obtained and the transition-state parameters for this barrierless process were evaluated canonically for each temperature and critical separation,  $r^\#(T)$ , based on the maximum Gibbs free energy criterion as described previously for radical-radical reactions.<sup>27,28</sup> The computed direct abstraction rate constant is shown as a dotted line in Figure 3; the result can be expressed by  $k_1 = 1.53 \times 10^{-13} T^{1.1} \exp(118/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . For those indirect channels that can produce Cl<sub>2</sub> + ClOO via **TS2**, **TS3**, and **TS4** with barriers of 3.5, 3.4, and 2.8 kcal/mol above the reactants, the smallest frequency vibration (less than 50 cm<sup>-1</sup>) in these TSs was treated as a free rotation and the reduced moment of inertia was approximately determined to be 201.7 amu. The sum of the rate constants for these indirect Cl<sub>2</sub>-formation paths,  $k_1'$ , shown as a dashed-dotted line in Figure 3, is minor at room temperature, amounting to less than 0.1% of Cl<sub>2</sub> yield at 298 K, but it increases to about 46% at 1000 K. The indirect abstraction rate constant for the formation of Cl<sub>2</sub> + ClOO can be expressed as  $k_1' = 7.14 \times 10^{-12} T^{0.86} \exp(-2370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in the temperature range of 200–1000 K.

**ClO + ClOCl Formation.** Besides the above paths, **LM1** and **LM2** can also dissociate to produce ClO + ClOCl via **TS5** and **TS6**. The vibration with the smallest frequency in these two transition states was also treated as a free internal rotator, and the reduced moment of inertia was determined to be 1124 amu. The predicted rate constant of  $k_2$  is shown as a dashed line in Figure 3, which can be expressed by  $k_2 = 2.19 \times 10^{-14} T^{0.70} \exp(-1110/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , covering the temperature range of 200–1000 K. The total rate,  $k_t = k_1 + k_1' + k_2$ , is shown as a thick solid line in Figure 3. The ratios of  $k_2/k_t$  are 0.04, 0.19, 0.55, and 0.62 at 200, 298, 500, and 1000 K, respectively. Apparently, over 298 K, formation of the ClO +

CIOCl products becomes quite significant and competitive. The predicted total rate constant is in reasonable agreement with available experimental data<sup>10,11,29</sup> in which Cl<sub>2</sub> + CIO were assumed to be the only products. The predicted rate constant above room temperature needs further experimental substantiation.

#### IV. Concluding Remarks

The kinetics and mechanism for the reaction of Cl with CIOCl has been investigated at the G2M//G96LYP/6-311+G-(3df) level of theory in conjunction with statistical rate constant calculations. A new product channel giving ClO + CIOCl was found. The total rate constant experimentally determined for Cl + CIOCl could be reasonably accounted for theoretically. At lower temperatures, the direct abstraction channel forming Cl<sub>2</sub> + CIO is dominant; over 298 K, formation of ClO + CIOCl becomes very competitive.

**Acknowledgment.** This work is sponsored by the Office of Naval Research under Contract No. N00014-89-J1949, Dr. J. Goldwasser, program manager. M.C.L. acknowledges the Taiwan National Science Council for the award of a distinguished visiting professorship.

#### References and Notes

- (1) Rowland, F. S.; Molina, M. J. *Rev. Geophys. Space Phys.* **1975**, *78*, 5341. Rowland, F. S. *Annu. Rev. Phys. Chem.* **1991**, *42*, 731. Johnston, H. S. *Annu. Rev. Phys. Chem.* **1992**, *43*, 1.
- (2) Molina, L. T.; Molina, M. J. *J. Phys. Chem.* **1987**, *91*, 433. Molina, M. J.; Tso, T. L.; Molina, L. T.; Wang, F. C.-Y. *Science* **1987**, *238*, 1253.
- (3) Barrett, J. W.; Solomon, P. M.; De Zafra, R. L.; Jaramillo, M.; Emmons, L.; Parrish, A. *Nature* **1988**, *336*, 455.
- (4) Molina, M. J.; Colussi, A. J.; Molina, L. T.; Schindler, R. N.; Tso, T. L. *Chem. Phys. Lett.* **1990**, *173*, 310.
- (5) DeMore, W. B.; Tschuikow-Roux, E. *J. Phys. Chem.* **1990**, *94*, 5856.
- (6) Toniolo, A.; Granucci, G.; Inglese, S.; Persico, M. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4266.
- (7) Kaledin, A. L.; Morokuma, K. *J. Chem. Phys.* **2000**, *113*, 5750.
- (8) Moore, T. A.; Okumura, M.; Seale, J. W.; Minton, T. K. *J. Phys. Chem. A* **1999**, *103*, 1691.
- (9) Jacobs, J.; Kronberg, M.; Mueller, H. S. P.; Willner, H. *J. Am. Chem. Soc.* **1994**, *116*, 1106.
- (10) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, *26*, 521.
- (11) Cox, R. A.; Hayman, G. D.; *Nature (London)* **1988**, *332*, 796.
- (12) Zhu, R. S.; Lin, M. C. *PhysChemComm* **2001**, *25*, 1.
- (13) Zhu, R. S.; Xu, Z. F.; Lin, M. C. *J. Chem. Phys.* **2002**, *116*, 7452.
- (14) (a) Zhu, R. S.; Lin, M. C. *J. Phys. Chem. A* **2002**, *106*, 8390. (b) Zhu, R. S.; Lin, M. C. *J. Chem. Phys.* **2003**, *118*, 4094.
- (15) Xu, Z. F.; Zhu, R. S.; Lin, M. C. *J. Phys. Chem. A* **2003**, *107*, 1040.
- (16) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785. (b) Gill, P. M. W. *Mol. Phys.* **1996**, *89*, 433.
- (17) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.
- (18) Mebel, A. M.; Morokuma, K.; Lin, M. C. *J. Chem. Phys.* **1995**, *103*, 7414.
- (19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (20) Klippenstein, S. J.; Wagner, A. F.; Dunbar, R. C.; Wardlaw, D. M.; Robertson, S. H. *VARIFLEX*, version 1.00; 1999.
- (21) Mokrushin, V.; Bedanov, V.; Tsang, W.; Zachariah, M. R.; Knyazev, V. D. *ChemRate*, version 1.19; National Institute of Standards and Technology: Gaithersburg, MD, 2002.
- (22) Nickolaissen, S. L.; Friedl, R. R.; Sander, S. P. *J. Phys. Chem.* **1994**, *98*, 155.
- (23) Chase, M. W., Jr. *NIST-JANAF Thermochemical Tables*, 4th ed.; J. Phys. Chem. Ref. Data, Monograph 9; American Chemical Society and American Institute of Physics for the National Institute of Standards and Technology: Washington, DC, 1998.
- (24) Lee, T. J.; Rohlfing, C. M.; Rice, J. E. *J. Chem. Phys.* **1992**, *97*, 6593.
- (25) McGrath, M. P.; Clemmshaw, K. C.; Rowland, F. S.; Hehre, W. J. *Geophys. Res. Lett.* **1988**, *15*, 883.
- (26) Li, W. K.; Ng, C. Y. *J. Phys. Chem. A* **1997**, *101*, 113.
- (27) Hsu, C.-C.; Mebel, A. M.; Lin, M. C. *J. Chem. Phys.* **1996**, *105*, 2346.
- (28) Chakraborty, D.; Hsu, C.-C.; Lin, M. C. *J. Chem. Phys.* **1998**, *109*, 8889.
- (29) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *JPL Publ.* **1997**, 97-4.