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Ab Initio Studies of ClO_x Radical Reactions: V. Evidence for a New Path in the Cl + ClOOCl Reaction

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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_2 + ClOO and Cl_2O + 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) cm^3 molecule^{-1} 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) cm^3 molecule^{-1} s^{-1}, accounting for less than 0.1% of the Cl_2 yield at 298 K but increasing to about 46% at 1000 K. The new Cl_2O + 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) cm^3 molecule^{-1} s^{-1} covering the temperature range of 200−1000 K. Above room temperature, Cl_2O formation becomes competitive; for example, its branching ratios, k_2/k_t, 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 $\Delta_f H^\circ_0$(ClOOCl) = 30 ± 2 kcal/mol.

I. Introduction

Chlorine peroxide (ClOOCl), formed by the recombination of ClO radicals, plays a pivotal role in the O_3-destruction chemistry.[1−3] Its photodissociation reaction in the stratosphere regenrates Cl atoms and, to some extent, ClO radicals depending on the wavelength.[4−9] The reaction of ClOOCl with Cl is known to be very fast with the production of Cl_2 and ClOO exclusively,[10,11]

$$Cl + ClOOCl \rightarrow Cl_2 + ClOO \qquad (1)$$

In principle, another exothermic product pair, Cl_2O + 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:

$$Cl + ClOOCl \rightarrow Cl\cdots O(Cl)OCl \rightarrow Cl_2O + ClO \qquad (2)$$

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_x reactions in this laboratory.[12−15]

II. Computational Methods

The geometries of the reactants, intermediates, transition states, and products of the Cl + ClOOCl reaction are computed at the G96LYP/6-311+G(3df) level with Barone and Adamo's Becke-type one-parameter functional using Gill96 exchange and LYP correlation.[16] 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[17] 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,[18] 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.[19]

The rate constants were computed with a microcanonical variational Rice−Ramsperger−Kassel−Marcus (RRKM) approach using the Variflex[20] and ChemRate codes.[21]

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 ^3O + OClO system,[14] 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

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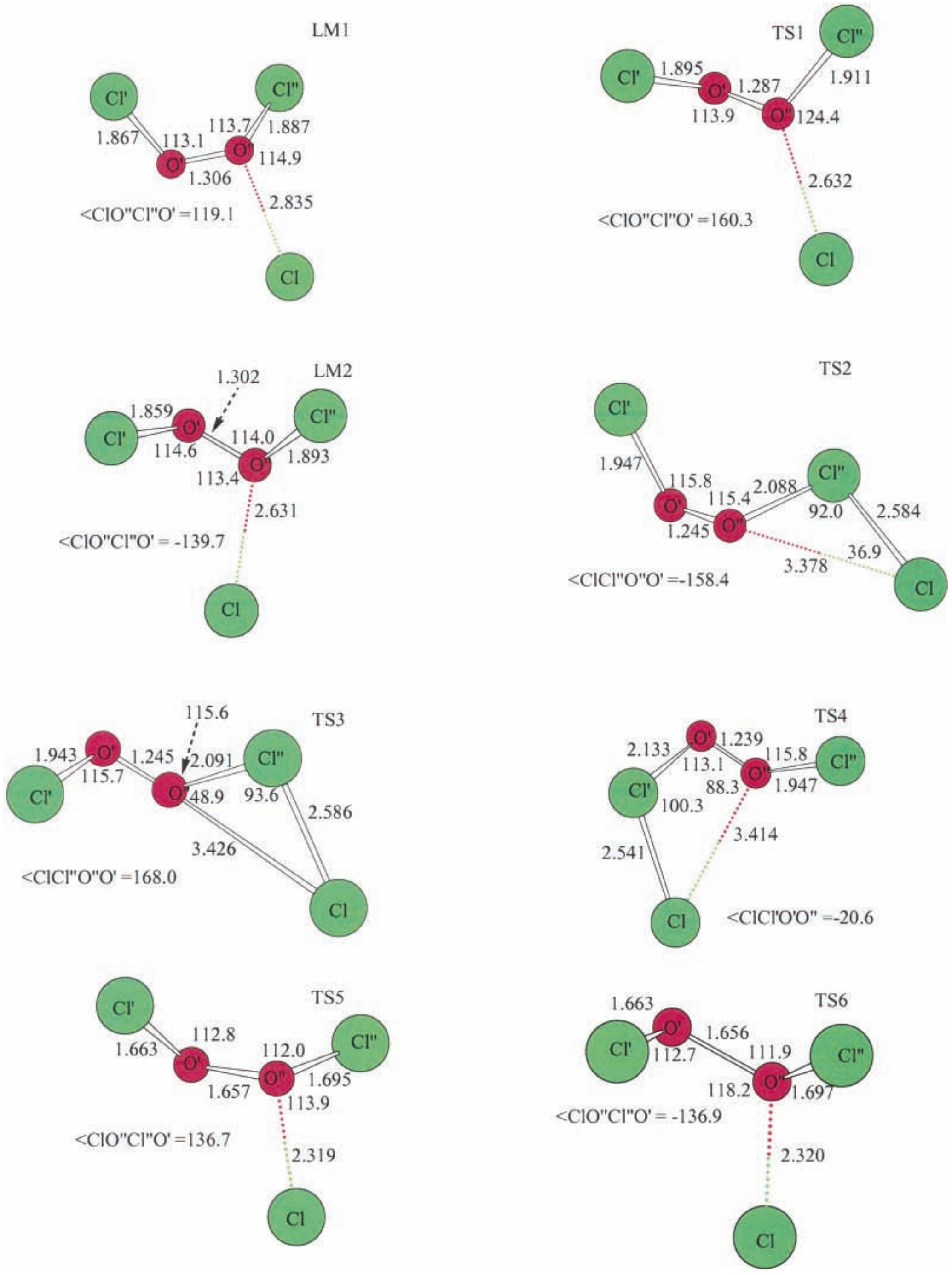

Figure 1. The optimized geometry of intermediates and transition states computed at the G96LYP/6-311+G(3df) level for the Cl + ClOOCl reaction.

structures are 0.86, 1.71, 14.3, 14.6, and 8.4 kcal/mol, respectively. From our previous calculation,[14] 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 ± 0.9 and 31.7 ± 0.7 kcal/mol based on the reactions Cl + ClOOCl → ClO + ClOCl and Cl + ClOOCl → Cl_2 + ClOO, respectively. These results are close to the experimental values, 29.7[22] and 32.6[11] kcal/mol and to our previously predicted value, 29.4 kcal/mol.[14b] 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_2 + ClOO Products. As discussed previously,[14b] among the five isomers of Cl_2O_2, the ClOOCl molecule with C_2 symmetry is most stable. Experimentally,[10,11] the Cl_2-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.

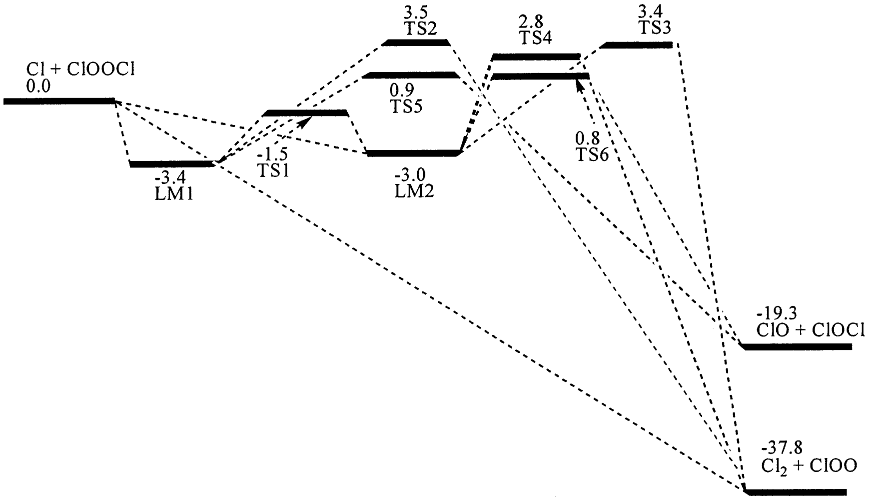

Figure 2. The schematic energy diagram for the Cl−ClOOCl system computed at the G2M level.

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^{-1})
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	91***i***, 42, 67, 117, 227, 350, 489, 521, 971
TS2	7.1, 0.7, 0.7	70***i***, 37, 83, 178, 226, 314, 429, 529, 1182
TS3	5.0, 0.8, 0.8	83***i***, 20, 94, 185, 219, 318, 424, 531, 1180
TS4	3.0, 1.2, 1.0	139***i***, 41, 90, 186, 237, 319, 377, 530, 1209
TS5	2.5, 1.5, 1.0	222***i***, 45, 92, 119, 190, 268, 398, 602, 711
TS6	2.5, 1.5, 1.0	225***i***, 45, 93, 119, 189, 269, 389, 602, 710

As shown in Figure 2, several reaction paths can lead to the abstraction products, Cl_2 + 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 attacts one of the Cl in ClOOCl, it directly leads to Cl_2 + ClOO barrierlessly with the exothemicity 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_2 + 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_3-destruction chemistry, we have examined the heat of formation of ClOOCl in greater detail. Based on the experimental heats of formation[23] for Cl, ClO, ClOCl, and ClOO and the predicted enthalpy changes for the two reactions

$$\mathrm{Cl + ClOOCl \rightarrow ClO + ClOCl}, \quad \Delta_r H^\circ_0 = -19.3 \text{ kcal/mol}$$

$$\mathrm{Cl + ClOOCl \rightarrow Cl_2 + ClOO}, \quad \Delta_r H^\circ_0 = -37.8 \text{ kcal/mol}$$

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[22] and 32.1 kcal/mol,[11] and are close to some of the previous theoretical estimates, 34.2[24] and 32.6[25] 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[14b] and 30.6,[26] 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,[14b] 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 ClOOCl at 0 K Based on Different Reactions and Methods with Available Data

reaction	$\Delta_f H^\circ_0$
(1) $ClO + ClO = ClOOCl$	29.4[14b]
(2) $Cl + ClOOCl = Cl_2 + ClOO$	32.9 ± 0.7[a], 26.1[b], 33.6[c], 31.7 ± 0.7[d]
(3) $Cl + ClOOCl = ClOCl + ClO$	34.3 ± 0.5[a], 29.9 ± 0.5[b], 29.6 ± 0.5[c], 33.9 ± 0.5[d]
(4) $HO + ClOOCl = HOOCl + ClO$[e]	29.3 ± 0.5[b]
(5) $HO_2 + ClOOCl = HOOCl + ClOO$[e]	28.2 ± 1.5[b]
(6) $H + ClOOCl = HOOCl + Cl$[e]	31.4[b]
(7) $HOOCl + HCl = H_2 + ClOOCl$[e]	30.7[b]
(8) $HOOCl + HOCl = H_2O + ClOOCl$[e]	31.9[b]
(9) $HOOH + Cl_2 = H_2 + ClOOCl$	28.3[b]
(10) $ClOOCl + H_2O = ClOCl + HOOH$	32.1 ± 0.5,[b] 32.6 ± 3.2,[25] 34.2,[24] [f] 30.6,[26] 29.7,[22] 32.1[11]

[a] G2M//G96/6-311+G(3df), this work. [b] G2M//B3LYP/6-311+G(3df), this work. [c] G96/6-311+G(3df), this work. [d] G2M//PW91PW91/6-311+G(3df), this work. [e] The heat of formation of HOOCl, 0.78 ± 0.5 kcal/mol, used in the reactions 4−8, is based on the reaction of $HOOH + HOCl = HOOCl + H_2O$ at the G2M(CC2)//B3LYP/6-311+G(3df,2p) level; the heats of formation of other species are taken from ref 23. [f] This value becomes 32.6 ± 1 kcal/mol if the most recent heat of formation for Cl_2O was used, as discussed in ref 14b.

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

Scheme 1

$Cl + ClOOCl \leftrightarrow$ **LM1*** $\rightarrow$ **LM1** (+M)
$\rightarrow ClO + ClOCl$
$\rightarrow Cl_2\ (ClCl'') + ClOO\ (Cl'OO)$
$\leftrightarrow$ **LM2*** $\rightarrow Cl + ClOOCl$
$\rightarrow ClO + ClOCl$
$\rightarrow Cl_2\ (ClCl'') + ClOO\ (Cl'OO)$
$\rightarrow Cl_2\ (ClCl') + ClOO\ (Cl''OO)$
$\rightarrow$ **LM2** (+M)

Scheme 2

$Cl + ClOOCl \leftrightarrow$ **LM2*** $\rightarrow$ **LM2** (+M)
$\rightarrow ClO + ClOCl$
$\rightarrow Cl_2\ (ClCl'') + ClOO\ (Cl'OO)$
$\rightarrow Cl_2\ (ClCl') + ClOO\ (Cl''OO)$
$\leftrightarrow$ **LM1*** $\rightarrow Cl + ClOOCl$
$\rightarrow ClO + ClOCl$
$\rightarrow Cl_2\ (ClCl'') + ClOO\ (Cl'OO)$
$\rightarrow$ **LM1** (+M)

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 required for the stabilization of ClO(Cl)OCl (**LM1** and **LM2**) were assumed to be approximately the same as that of ClOOCl.[14b]

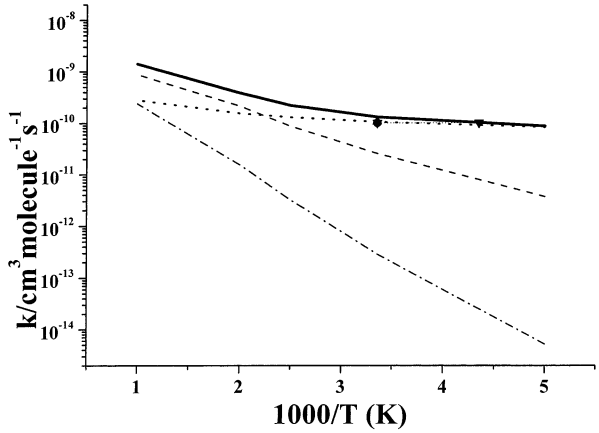

Figure 3. Comparison of the predicted rate constants with the experimental values in N_2. Dotted and dashed−dotted lines represent the predicted formation rate constants of $Cl_2 + ClOO$, k_1 and k_1', respectively. Dashed line represents k_2 for $ClO + ClOCl$ formation, and the thick solid line represents the total rate constant. Symbols are experimental data of ref 11.

$Cl_2 + ClOO$ Formation. As alluded to in the preceding discussion on the results of ab initio calculations, $Cl_2 + ClOO$ 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 $Cl_2 + ClOO$ 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.[27,28] The computed direct abstraction rate constant is shown as a dotted line in Figure 3; the result can be expressed by $k_1 = 1.53 \times 10^{-13} T^{1.1} \exp(118/T)$ cm^3 molecule^{-1} s^{-1}. For those indirect channels that can produce $Cl_2 + ClOO$ 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^{-1}) 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_2-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_2 yield at 298 K, but it increases to about 46% at 1000 K. The indirect abstraction rate constant for the formation of $Cl_2 + ClOO$ can be expressed as $k_1' = 7.14 \times 10^{-12} T^{0.86} \exp(-2370/T)$ cm^3 molecule^{-1} 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 $k_2 = 2.19 \times 10^{-14} T^{0.70} \exp(-1110/T)$ cm^3 molecule^{-1} 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 +

ClOCl products becomes quite significant and competitive. The predicted total rate constant is in reasonable agreement with available experimental data[10,11,29] in which Cl_2 + ClOO 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 ClOOCl 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 + ClOCl was found. The total rate constant experimentally determined for Cl + ClOOCl could be reasonably accounted for theoretically. At lower temperatures, the direct abstraction channel forming Cl_2 + ClOO is dominant; over 298 K, formation of ClO + ClOCl becomes very competitive.

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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) Nickolaisen, 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.; Clemitshaw, 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.