Ab Initio Studies of ClO\textsubscript{x} Reactions: I. Kinetics and Mechanism for the OH + ClO Reaction

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Abstract. The reaction of OH with ClO has been investigated by ab initio molecular orbital and variational transition state theory calculations. Both singlet and triplet potential energy surfaces predicted by the G2M method are presented. The reaction was shown to take place primarily over the singlet surface by two main channels producing HO\textsubscript{2} + Cl and HCl + O\textsubscript{2} (\textsuperscript{1}\textDelta), with the former being dominant. The predicted total rate constant, \( k_1 = 5.27 \times 10^{-9} \, T^{-1.03} \exp(-40/T) \, \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \), and product branching ratios in the temperature range 200 – 500 K at P < 200 atm agree satisfactorily with experimental values. The computed branching ratios, \( k_2/(k_1+k_2) = 0.073 \) for HCl + \textsuperscript{1}\textO\textsubscript{2} and 0.045 – 0.048 for DCl + \textsuperscript{1}\textO\textsubscript{2} in the temperature range 200 – 500 K based on the recent experimental heat of formation for HO\textsubscript{2} (4.0 ± 0.8 kcal/mol) compare closely with the experimental values, 0.07 ± 0.03 and 0.05 ± 0.02, respectively. At higher temperatures (1000 – 2500 K), the branching ratios increase slightly to 0.084 – 0.137 and 0.061 – 0.111 for the OH and OD reactions, respectively. The rate constant for HO\textsubscript{2} + Cl and HCl + O\textsubscript{2} production from OH + ClO in the temperature range, 500 – 2500 K, can be given by \( k_1 = 3.4 \times 10^{13} \, T^{0.3} \exp(725/T) \) and \( k_2 = 5.85 \times 10^{19} \, T^{1.67} \exp(1926/T) \, \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \), respectively.

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I. INTRODUCTION
Chlorine oxide radicals play a key role in the destruction of stratospheric ozone.\textsuperscript{1,2} There have been extensive experimental studies on the kinetics of ClO\textsubscript{x} formation and reactions with atmospheric species in conjunction with computer simulation of ozone depletion by freons.\textsuperscript{2} Theoretically, there have been only limited studies on the chemistry of ClO\textsubscript{x} reactions, particularly for quantitative prediction of absolute reaction rates and product branching ratios.

In this series of computational studies, we focus on the chemistry of ClO\textsubscript{x} reactions with atmospheric species with special emphases on their detailed mechanisms through careful mapping of the potential energy surfaces involved. Individual rate constants and product branching probabilities will be predicted with statistical theories appropriate for the type of the systems investigated and compared with available experimental data.

For the title reaction, there have been numerous studies on its rate constants at the pressures of interest to the stratospheric chemistry.\textsuperscript{3-13} The reaction may occur by the following mechanism with the two key product channels:

\begin{align*}
\text{OH} + \text{ClO} & \rightarrow \text{HO}_2 + \text{Cl} \\
& \rightarrow \text{HCl} + \text{O}_2
\end{align*}

HOOC\textsubscript{1} has been assumed to be the key intermediate leading to the formation of these two sets of products.\textsuperscript{14} Reaction (1) has been shown to be the major channel in the reaction.\textsuperscript{3-6} In these studies, the branching ratio \(k_2/(k_1+k_2)\) was reported in the range of \(6.5 -10\, \%\); but the products of reaction (2) were not directly measured. Recently, there are several measurements of HCl or DCl, the branching ratio \(k_2/(k_1+k_2)\) for the two product channels have been determined. Lipson et al.\textsuperscript{9,10} reported the branching ratio \(k_2/(k_1+k_2)\) of 7 ± 3\,\% for OH + ClO and 5 ± 2\,\% for OD + ClO reactions, respectively; Bedjania et al.\textsuperscript{12} obtained \(k_2/(k_1+k_2) = 3.5 \pm 1\,\%\) for the OH + ClO reaction. Direct measurement of the concentration of [HCl] and [OH] in the reaction by Wang and Keyser\textsuperscript{13} found that the yield of HCl from the OH + ClO reaction, given by \([\text{HCl}]/[\text{OH}]_0\), was 9.0 ± 4.8 \,\% independent of temperature between 218 and 298 K at 1 Torr pressure.

Theoretically, the stability of HOOC\textsubscript{1} intermediate and its structural isomers have been studied by Francisco et al.\textsuperscript{15} and Lee and Rendell.\textsuperscript{16} Sumathi and Peyerimhoff\textsuperscript{17} calculated the potential energy surface (PES) of the reaction and concluded that reaction (2) was less important because of the high barrier. Dubey et al.\textsuperscript{18} performed a box-model sensitivity analysis using the recommended value\textsuperscript{19} of \(k_1\) and found that the transition state (see TS5 in Fig.3 later) for HCl production must lie at least 2 kcal/mol below the reactants for the HCl yield to exceed 5\,\%; Lipson et al.\textsuperscript{10} performed a statistical theory calculation by adjusting the energy of TS5 to reproduce their results; they arrived at the conclusion that TS5 should locate at ~1.2 kcal/mol below the reactants.

In the present work, we attempt to map out the complete PES for the system and carry out the total rate constant and branching ratio calculations for the title reaction on the basis of the computed PES using a variational statistical method. The results of this study are presented herein.

II. COMPUTATIONAL DETAILS
The geometry of the reactants, products, intermediates and transition states of the title reactions have been fully optimized by using the hybrid density functional B3LYP
method (Becke's three-parameter nonlocal exchange functional$^{20-22}$ with the correlation functional of Lee, Yang, and Parr$^{23}$) with the 6-311+G(3df, 2p) basis set. Vibrational frequencies employed to characterize stationary points, zero-point energy (ZPE) corrections have also been calculated at this level of theory, and have been used for the coupled rate constant calculations. All the stationary points have been positively identified for local minima (with the number of imaginary frequencies $N_{IMAG} = 0$) and transition states (with $N_{IMAG} = 1$). Intrinsic reaction coordinate (IRC) calculations$^{24}$ have been performed to confirm the connection of each transition state with designated intermediate.

The total G2M energy with zero-point energy (ZPE) correction is calculated as follows:$^{25}$

\[
E[(G2M(CC2)] = E_{bas} + \Delta E(+) + \Delta E(2df) + \Delta E(CC) + \Delta' + \Delta E (HLC, CC2) + ZPE (3df 2p).
\]

\[
E_{bas}= E[PMP4/6-311G(d, p)]
\]

\[
\Delta E(+) = E[PMP4/6-311+G(d, p)] - E_{bas}
\]

\[
\Delta E(2df) = E[PMP4/6-311G(2df,p)] - E_{bas}
\]

\[
\Delta E(CC) = E[CCSD(T)/6-311G(d, p)] - E_{bas}
\]

\[
\Delta' = E[UMP2/6-311 + G(3df,2p)] - E[UMP2/6-311 + G(2df,p)] - E[UMP2/6-311(d,p)]
\]

\[
\Delta E (HLC, CC2) = -5.78n_\beta - 0.19n_\alpha \text{ in units of mhartree.}
\]

where $n_\alpha$ and $n_\beta$ are the numbers of valence electrons, $n_\alpha \geq n_\beta$. All calculations were carried out with Gaussian 98.$^{26}$

The rate constants were computed with a microcanonical variational RRKM (Variflex$^{27}$) code which solves the master equation$^{28,29}$ involving multi-step vibrational energy transfers for the excited intermediate HOOC.$^\dagger$. The energies for the intermediates and transition states calculated at the G2M (CC2) level were used in the calculation. Similar to our previous calculations$^{30-32}$ with the Variflex code, the component rates were evaluated at the E, J-resolved level. In order to achieve convergence in the integration over the energy range, an energy grain size of 20 cm$^{-1}$ was used for the temperature range 200 – 500 K, and 100 cm$^{-1}$ for the temperature range 1000 – 2500 K. These grain sizes provide numerically converged results for all temperatures studies with the energy spanning range from 12447 cm$^{-1}$ below to 67000 cm$^{-1}$ above the threshold. The total angular momentum $J$ covered the range from 1 to 241 in steps of 10 for the E, J-resolved calculation. For the barrierless transition states, the Morse potential,

\[
E (R) = D_e [1 - e^{-\beta (R - R_e)}]^2
\]

was used to represent the potential energy along the minimum energy path of each individual reaction coordinate. In the above equation, $R$ is the reaction coordinate (i.e. the distance between the two bonding atoms; O-O or O-Cl in this work), $D_e$ is the bond energy excluding zero-point energy and $R_e$ is the equilibrium value of $R$. For the tight transition states, the numbers of states were evaluated according to the rigid-rotor harmonic-oscillator approximation.

III. RESULTS AND DISCUSSION
A. Potential Energy Surfaces and Reaction Mechanism

The geometry of the reactants, intermediates and products optimized at the B3LYP/6-311+G(3df, 2p) level is shown in Fig.1, while those of the transition states
optimized at the same level are displayed in Fig.2. The singlet and triplet potential energy diagrams obtained at the G2M (CC2) level are presented in Figs. 3 and 4; the total and relative energies of the singlet and triplet species involved in the reaction are compiled in Table 1 and the vibrational frequencies and moments of inertia of the species are summarized in Table 2.

a). Singlet Reaction Channels

**HOOC\textsubscript{1}, HOC\textsubscript{1}O and HClO\textsubscript{2} intermediates and their isomerization.** The two O atoms of the OH and ClO radicals approach one another to form HOOC\textsubscript{1} with C\textsubscript{1} symmetry as shown in Fig.1. The dihedral angle at the B3LYP/6-311+G(3df, 2p) level of theory is predicted to be 88.7°, which is close to the values of 88.4, 88.2 and 89.1° obtained by Sumathi and Peyerimhoff, Francisco et al. and Lee and Rendell, respectively, at the B3LYP/6-311++G(2df,2pd), MP2/6-311G(2d,2p) and CCSD(T)/TZ2P levels. The Cl-O bond length in HOOC\textsubscript{1} is 1.730 Å, which can be compared with the values: 1.738, 1.740, and 1.758 Å, reported in ref. 17 at the B3LYP/6-311+G(2df, 2pd), MP2(FU)/6-311+G(d, p) and CAS (12, 12)/6-31G(d, p) levels, and the values: 1.739, 1.751, 1.750 and 1.746 Å, reported in refs. 15 and 16 at the MP2/6-31G(d), MP2/6-311G(d, p), MP2/6-311G(2d, 2p) and CCSD(T)/TZ2P levels, respectively. The calculated O-O bond length, 1.410 Å, is also close to the values of 1.409, 1.416 Å obtained at the B3LYP/6-311++G(2df,2pd) and MP2(FU)/6-311++G(d, p), but it is about 0.03 Å shorter than those obtained at CCSD(T)/TZ2P and CAS(12, 12)/6-31G(d, p). Apparently, the HOOC\textsubscript{1} structural parameters are sensitive to the methods employed. At the G2M(CC2)//B3LYP/6-311+(3df,2p) level, HOOC\textsubscript{1} lies below the reactants by 35.6 kcal/mol, which is about 8 and 4 kcal/mol lower than those obtained at the B3LYP/6-311++G(2df, 2pd) and MP2/6-311G(2d,2p) levels.

Besides the HOOC\textsubscript{1} structure, there are two other isomers, HOC\textsubscript{1}O and HClO\textsubscript{2}. In HOC\textsubscript{1}O (chlorous acid), the OCl and ClO bond lengths are different. The OCl bond length shows stronger basis-set and electron-correlation effects than that of the ClO bond. For instance, O-Cl bond length predicted at the B3LYP/6-311+(3df, 2p) level is 1.707 Å; however, at the B3LYP/6-311++G(2df,2pd), MP2/6-311G(2d,2p), CAS (12, 12)/6-31G(d, p) levels of theory, it was predicted to be 1.719, 1.752, 1.755 and 1.1768 Å, respectively. The ClO bond length predicted by the corresponding five methods are 1.507, 1.517, 1.503, 1.536 and 1.543 Å, respectively. HOC\textsubscript{1}O lies below the reactants by 28.6 kcal/mol, almost 9 kcal/mol less stable than HOOC\textsubscript{1}, which can isomerize to HOC\textsubscript{1}O via TS1 (see Fig. 2). TS1 shows a loose structure, the breaking O-O and the forming O-Cl bond lengths, 2.131 Å and 2.243 Å, are consistent with the corresponding bond lengths 2.140 and 2.243 Å predicted at the B3LYP/6-311++G(2df, 2pd) level. The isomerization barrier is 39.3 kcal/mol at the G2M level, which is about 12 kcal/mol lower than that predicted at the B3LYP/6-311++G(2df, 2pd) level of theory. The difference mainly arises from the coupled cluster correction and “higher level correction” included in the G2M(CC2) method.

The third isomer, HClO\textsubscript{2}, has C\textsubscript{2v} symmetry. In HClO\textsubscript{2}, the Cl-O bond length is 0.261 Å shorter than that in HOOC\textsubscript{1} and 0.038 Å shorter than the terminal Cl-O bond length in HOC\textsubscript{1}O, probably because of the resonance effects in HClO\textsubscript{2}. This isomer lies above the reactants by 13.6 kcal/mol. The isomerization between HOC\textsubscript{1}O and HClO\textsubscript{2} has large, 67.6 kcal/mol barrier, as shown in TS2 of Fig. 2. The stability of these three isomers based on
our calculation is HOOCI > HOCIO > HClO₂. The energies of HClO₂ and HOCIO relative to HOOCI at the G2M level, 49.2 and 7.0 kcal/mol, are consistent with these values, 47.5 ± 1.8 and 6.3 ± 1 kcal/mol, predicted at the CCSD(T)/ANO4 level (the ANO4 basis set consists of 6s5p3d2f1g, 5s4p3d2f1g and 4s3p2d1f atomic natural orbital (ANO)).

**HOO + Cl formation.** The formation of HOO + Cl is the main experimentally observed channel as mentioned in the previous section. It is formed by the barrierless dissociation of HOOCI. Interestingly, HOOCI can also form HOO + Cl via a tight transition state TS3, in which the H atom migrates from the OH group to the O adjacent to the Cl atom, with the simultaneous elimination of the Cl atom. If we label HOOCI as HO₃O₂Cl, the barrierlessly dissociation channel produces HO₁O₂ + Cl, whereas the channel via TS3 produces HO₂O₁ + Cl. TS3 lies above the reactants by 19.3 kcal/mol. The other transition state leading to HOO + Cl is TS4, where the ClOO angle bends from 110.2° in HOOCI to 59.2° in TS4 and the Cl-O bond lengths by about 0.4 Å, resulting in a three-member-ring transition state to form HOO + Cl. TS4 lies above the reactants by 33.6 kcal/mol. Apparently, the latter two pathways are kinetically unimportant. The exothermicity for the formation of the HOO + Cl products, is 2.8 kcal/mol, which is close to 2.3 and 1.0 kcal/mol obtained by other investigators.

**HCl + ¹O₂ formation.** This channel can occur from HOOCI via a four-center transition state TS5. In TS5, the H atom transfers from the O atom of the HO group to the Cl atom. The OOCl angle bends from 110.2° in HOOCI to 78.4° in TS5; the breaking Cl-O bond increases from 1.730 Å in HOOCI to 2.618 Å; the forming HCl bond is 1.899 Å. The structure parameters of this transition state is similar to that obtained by Sumathi and Peyerimhoff at the B3LYP/6-311++G(2df, 2pd) but different from that obtained at the QCISD/cc-pVDZ level. At the QCISD/cc-pVDZ level, the breaking Cl-O and the forming H-Cl bond lengths, and the OOCl bond angle in TS5 are 2.66, 2.36 Å and 85°, respectively. The barrier height at TS5 relative to HOOCI at the G2M//B3LYP/6-311+G(3df, 2p) level is 33.5 kcal/mol, which is about 10 kcal/mol lower than the value of 43.1 cal/mol obtained at the B3LYP/6-311++G(2df, 2pd) level, but it is much closer to the value, 29.3 ± 3 kcal/mol, predicted by multireference CISD method. Similar results predicted by the G2M//B3LYP/6-311+G(3df, 2p) and the CASSCF methods for the formation of singlet ¹O₂ were also obtained for the H₂O + 2HO₂ reaction. The reaction producing HCl + ¹O₂ is exothemic by 30.2 kcal/mol based on our calculation.

It should be mentioned that the predicted TS5 energy, -2.1 kcal/mol relative to the reactants, agrees closely with the values –2 kcal/mol by Dubey et al. and –1.2 kcal/mol by Lipson et al. obtained by fitting experimentally observed branching ratios.

### b). Triplet Reaction Channels

**Trans-³HOOCI, cis-³HOOCI and ³HOCO intermediates and transition states TS6 and TS7.** The O atom of OH attacks the O atom of ClO from different directions can form triplet complexes, trans-³HOOCI and cis-³HOOCI, via transition states TS6 and TS7, with the HOO angles at 94.4° and 100.0°, respectively. Other parameters in these two transition states have rather minor differences (see Fig. 2). TS6 and TS7 lie above the reactants at 17.2 and 15.8 kcal/mol, respectively, which are evidently quite high. The trans- and cis- intermediates lie below the reactants by 4.8 and 7.8 kcal/mol at the G2M
level. In trans-\(^3\)HOOC\(_1\) and cis-\(^3\)HOOC\(_1\), the Cl-O bond lengths are 2.386 and 2.411 Å, respectively. Inspecting the structure of cis-\(^3\)HOOC\(_1\), one can see that there is intramolecular hydrogen bonding; the hydrogen bond length is 2.285 Å, this results in the higher stability of cis-\(^3\)HOOC\(_1\) than trans-\(^3\)HOOC\(_1\) by about 3 kcal/mol. In addition to these two intermediates, the H atom of OH attacks the O atom of ClO to form a four-member-ring complex \(^3\)HOClO via TS 8, which lies 17.9 kcal/mol above the reactants. The triplet \(^3\)HOClO complex lies above the reactants by 6.2 kcal/mol at the G2M level. At the B3LYP/6-311++G(2df, 2pd) level, \(^3\)HOClO and TS8 lie 11.4 and 9.7 kcal/mol above the reactants.

**HOO + Cl formation.** Besides the singlet channel, HOO + Cl can also be produced directly from cis–\(^3\)HOOC\(_1\) dissociation without an intrinsic barrier or from the decomposition of trans-\(^3\)HOOC\(_1\) via TS9, which is characteristically similar to the singlet TS3 involving the H-migration/Cl-elimination mechanism. TS9 lies 32.2 kcal/mol above the reactants. Even though triplet cis-HOOC\(_1\) can directly dissociate to form HOO + Cl, the high barrier for its formation as described above prevents the formation of HOO + Cl via the triplet surface.

**HCl + \(^3\)O\(_2\) formation.** As shown in Figs. 2 and 4, the cis - \(^3\)HOOC\(_1\) can form the ground state \(\text{O}_2\) and HCl via a four-center transition TS10 with Cs symmetry. The breaking Cl-O and the forming H-Cl bond lengths in TS10 are, respectively, 0.265 Å longer and 0.46 Å shorter than those in cis-\(^3\)HOOC\(_1\). TS10 lies below the reactants by 3.8 kcal/mol, which is 1.7 kcal/mol lower than that for the formation of HCl + \(^1\)O\(_2\) via the singlet HOClO intermediate. However, the large entrance barrier for the formation of cis-\(^3\)HOOC\(_1\) effectively prevents the formation of HCl + \(^3\)O\(_2\). Our calculations indicate that the experimentally observed HCl-elimination in the reaction of OH + ClO mainly arises from the singlet path as will be quantitatively illustrated by the predicted branching rate constants.

**HOCl + \(^3\)O formation.** There are two possible channels for the production of HOCl + \(^3\)O: the barrierless dissociation of \(^3\)HOClO and the dissociation of the trans-HOClO dissociates via a three-centered transition state TS11 with a barrier height of 31.4 kcal/mol. Comparing TS9 with TS11, one can see that in TS9 the H atom migrates from one O atom to other accompanied by Cl-atom elimination; whereas in TS11, the H atom migrates from the connecting O atom to another followed by the elimination of the first O atom. Both channels are unfavorable on account of the high entrance barriers.

### B. Rate Constant Calculations

Variational TST and RRKM calculations have been carried out for the rate constant of this reaction with the Variflex code\(^{27}\) by including the following channels:

\[
\text{OH} + \text{ClO} \rightarrow \text{HOCl}^+ \rightarrow \text{HO}_2 + \text{Cl} \quad \text{(1)}
\]

\[
\rightarrow \text{HOCl}^+ \rightarrow \text{HCl} + \text{O}_2 \quad \text{(2)}
\]

The energies used in the calculation are plotted in the Fig. 3 and the vibrational frequencies and moments of inertia are listed in Table 2. The L-J parameters required for the RRKM calculations for HOCl, \(\epsilon = 409\) K and \(\sigma = 3.1\) Å, were derived from deconvoluting the L - J potential of the He-HOCl system obtained by our ab initio calculation at the B3LYP/6-311+G(3df, 2p) level. The \(\epsilon\) and \(\sigma\) parameters for the He-HOCl collision pair were determined to be 64.0 K and 3.1 Å by fitting the L - J
function, \( V = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \). The L-J parameters for He, \( \varepsilon = 10 \) K and \( \sigma = 2.55 \) Å, were taken from the literature.\(^\text{35}\)

**a) Total Rate Constant for \( \text{OH} + \text{ClO} \)**

As aforementioned, the total rate constant (\( k_t = k_1 + k_2 \)) for the reaction has been measured by many investigators.\(^\text{3-13}\) Three groups obtained lower rate values at room temperature: they are \( 0.91 \pm 0.26 \), \( 1.17 \pm 0.33 \), and \( 1.19 \pm 0.09 \) cm\(^3\)molecule\(^{-1}\)s\(^{-1}\) by Leu and Lin,\(^\text{3}\) Ravishankara et al.,\(^\text{7}\) and Burrows et al.,\(^\text{4}\) respectively. The total rate constant was found to be temperature-independent in the temperature ranges of 243 – 335 K by Burrows et al.\(^\text{4}\) and Ravishankara et al.\(^\text{7}\) On the other hand, Hills and Howard\(^\text{5}\) reported a negative temperature dependence with \( E/R = - (235 \pm 46) \) K and \( k_t = 1.75 \pm 0.31 \) cm\(^3\)molecule\(^{-1}\)s\(^{-1}\) at room temperature. Similar negative-temperature dependent rate constants were obtained by Lipson et al.\(^\text{9}\) with \( E/R = - (292 \pm 72) \) and \( k_t = 1.46 \pm 0.23 \) cm\(^3\)molecule\(^{-1}\)s\(^{-1}\) at 298 K. In addition, Poulet et al.\(^\text{6}\) obtained \( k_t = 1.77 - 1.99 \) cm\(^3\)molecule\(^{-1}\)s\(^{-1}\) at room temperature. Kegley-Owen et al.\(^\text{11}\) reported a similar temperature coefficient, \( E/R = - (295 \pm 95) \) K, which is similar to that of ref. 9, but with \( k_t = 2.44 \pm 0.63 \) cm\(^3\)molecule\(^{-1}\)s\(^{-1}\) at 298 K. Bedjanian et al.\(^\text{12}\) measured the rate constants at 230 – 360 K, \( k_t = (6.7 \pm 1.8) \times 10^{-12} \exp(360 \pm 90)/T \) cm\(^3\)molecule\(^{-1}\)s\(^{-1}\) with \( k_t = (2.2 \pm 0.4) \times 10^{-11} \) cm\(^3\)molecule\(^{-1}\)s\(^{-1}\) at 298 K; their \( k_t \) at 298 K is much closer to the most recent value, \( 2.22 \pm 0.33 \) cm\(^3\)molecule\(^{-1}\)s\(^{-1}\) determined by Wang and Keyser\(^\text{13}\). In the following section, the rate constant calculation and results will be presented.

From ab initio calculations we see that the formation of HOO + Cl and HCl + O\(_2\) from the triplet path can be neglected because of the higher entrance barriers. Here we calculated the rate constants for the singlet reaction path. The association reaction of OH with ClO producing HOOCl occurs without a well-defined transition state due to the absence of an intrinsic reaction barrier. The flexible variational transition state approach originally developed by Marcus and co-workers\(^\text{36,37}\) has been employed by means of the Variflex code\(^\text{27}\) as alluded to above. The association potential energy for the approach of OH to ClO producing HOOCl was calculated by varying the forming Cl-O bond distance from its equilibrium value, 1.392 to 3.8 Å, with an interval of 0.1 Å. Other geometric parameters were fully optimized at the B3LYP/6-311G(d, p) level of theory. The calculated total energy at each point was fitted to a Morse potential energy function given previously and then scaled to match the dissociation energy predicted at the G2M/B3LYP/6-311+G(3df, 2p) level of theory. The value of \( \beta \) in the Morse potential was determined to be 3.52 Å\(^{-1}\). A similar calculation has been performed for the decomposition of HOOCl to HO\(_2\) + Cl, which also occurs without a well-defined transition state. The dissociation potential energy function was obtained by varying the breaking O - Cl bond from the equilibrium value, 1.801 Å, to 3.6 Å at an interval of 0.1 Å. The value of \( \beta \) in the Morse potential was determined to be 2.56 Å\(^{-1}\).

In order to establish the reliability of our calculation, experimental and predicted heats of formation for some species are compared in Table 3. It can be seen that for OCIO, CIOO, HOCl, the predicted heats of formation agree reasonably with the experimental values. However, the heat of formation for HO\(_2\), although agrees with the old value reported in JANAF\(^\text{38}\) (see Table 3), it is lower than the most recently obtained value, \( 4.0 \pm 0.8 \) kcal/mol,\(^\text{39}\) which is considered to be the most accurate one. In our rate constant calculation, both the predicted and the recent value are used. The theoretically predicted total rate constants in He are compared with available experimental data in Fig.
5. Inspection of the results presented in Fig. 5 using both the high and low values of \( \text{HO}_2 \) heat of formation shows that the predicted absolute rate constants with the He buffer gas has a negative temperature dependence which is consistent with the experimental measurements.\(^9\)\(^{-13}\) Based on our G2M PES, the predicted total rate constant, which is pressure-independent below 200 atm at 200 – 500 K, can be expressed by
\[
k_t = 1.24 \times 10^{-8} T^{-1.09} \exp(-99/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}.
\]
This result is also graphically presented in Fig. 5 as a thick dotted line with \( k_t = 1.81 \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1} \) at 298 K. The predicted total rate constant, consistent with some of the experimental results,\(^5\),\(^6\) lies between the lower\(^3\),\(^4\),\(^7\),\(^9\) and higher\(^11\),\(^12\),\(^13\)(b) experimental values. Based on the “most accurate” heat of formation of \( \text{HO}_2 \),\(^39\) we obtained \( k_t = 5.27 \times 10^{-9} T^{-1.03} \exp(-40/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1} \), which is plotted as a thick solid line in Fig. 5, with \( k_t = 1.31 \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1} \) at 298 K. The predicted \( k_t \) at 298 K is higher than the lowest experimental value\(^3\) by about a factor of 1.4 and lower than the highest experimental value\(^11\) by about a factor of 1.8. The results obtained at other temperatures are also compared with experimental values in Fig. 5. For comparison, the predicted rate constant for the formation of \( \text{HCl} + ^1\text{O}_2 \) is plotted in the figure as a thick dashed line; this result will be discussed in the following section.

b) Products Branching Ratios
Table 4 presents the computed \( k_2 \), \( k_t \) and the branching ratio \( k_2/(k_1+k_2) \) for \( \text{OH} + \text{ClO} \) and \( \text{OD} + \text{ClO} \) at 200 – 2500 K, based on \( \Delta_f \text{H}_0(\text{HO}_2) = 4.0 \text{ kcal/mol} \). The comparison for the predicted and experimental values are plotted in Fig. 6 (a) and (b) for \( \text{HCl} + \text{O}_2 \) and \( \text{DCl} + \text{O}_2 \) products, respectively. The solid lines are the predicted results using the best heat of formation for \( \text{HO}_2 \); dotted lines are those based on the G2M energies; symbols are the experimental values.\(^9\),\(^10\),\(^12\) The results show that the predicted branching ratio, \( k_2/(k_1+k_2) \), agrees better with experiment using the higher heat of formation of \( \text{HO}_2 \); the branching ratio is nearly constant in the temperature of 200 - 500 K for \( \text{HCl} + ^1\text{O}_2 \) and is slightly temperature dependent for \( \text{DCl} + ^1\text{O}_2 \) products (see Table 4). The predicted values, 7.3\% for \( \text{HCl} + ^1\text{O}_2 \) and 4.5 – 4.8\% for \( \text{DCl} + \text{O}_2 \), over the broad temperature range of 200 – 500 K, agree quantitatively with experimental results: 7 ± 3\% for \( \text{OH} + \text{ClO} \) and 5 ± 2\% for \( \text{OD} + \text{ClO} \) determined by Liposon et al.,\(^9\),\(^10\) but higher than that obtained by Bedjanian et al.,\(^12\) for the former reaction, 3.5 ± 1\%. At higher temperatures (1000 – 2500 K), the branching ratios increase slightly to 8.4 – 13.7\% for \( \text{HCl} + ^1\text{O}_2 \) and 6.1 – 11.1\% for \( \text{DCl} + ^1\text{O}_2 \). The absolute values of \( k_1 \) and \( k_2 \) for \( \text{OH} + \text{ClO} \) over the temperature range 500 – 2500 K can be given respectively in units of \( \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \) by
\[
\begin{align*}
\text{k}_1 &= 3.4 \times 10^{-13} T^{0.3} \exp(725/T) \\
\text{k}_2 &= 5.85 \times 10^{-19} T^{1.67} \exp(1926/T).
\end{align*}
\]

VI. CONCLUSION
The mechanism, rate constants and product branching ratios for the reaction of the ClO radical with OH and OD have been computed for the first time at the G2M level of theory in conjunction with variational RRKM calculations. The results agree closely with experimental findings in all respects. The reaction produces primarily \( \text{HOO} + \text{Cl} \) with the formation of \( \text{HCl} + ^1\text{O}_2 \) (not \( ^3\text{O}_2 \)) amounting to about 7\% over the broad temperature range of 200 – 500 K. For kinetic modeling, the rate constants for both branches of the reaction have been calculated and reported for a wide range of conditions.
V. ACKNOWLEDGEMENT
This work is sponsored by the Office of Naval Research under contract no. N00014 – 89 – J 1949, Dr. J. Goldwasser program manager.

VI. REFERENCES


Table 1. Total and relative energies\(^a\) of the reactants, intermediates, transition states and products for the reaction OH + ClO calculated at different levels of theory with the B3LYP/6-311+G(3df, 2p) optimized geometry.

<table>
<thead>
<tr>
<th>Species</th>
<th>ZPE(^b)</th>
<th>B3LYP/6-311+G (3df, 2p)</th>
<th>MP2/6-311+G(3df, 2p)</th>
<th>G2M</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO + CO</td>
<td>6.6</td>
<td>-611.1306334</td>
<td>-610.2972889</td>
<td>-610.4087163</td>
</tr>
<tr>
<td>HOOCl</td>
<td>10.6</td>
<td>-28.1</td>
<td>-42.0</td>
<td>-35.6</td>
</tr>
<tr>
<td>HOCIO</td>
<td>10.4</td>
<td>-21.3</td>
<td>-38.4</td>
<td>-28.6</td>
</tr>
<tr>
<td>HClO(_2)</td>
<td>9.8</td>
<td>20.8</td>
<td>1.7</td>
<td>13.6</td>
</tr>
<tr>
<td>trans-3HOOCl</td>
<td>10.0</td>
<td>-7.2</td>
<td>-7.0</td>
<td>-4.8</td>
</tr>
<tr>
<td>cis-3HOOCl</td>
<td>10.1</td>
<td>-11.9</td>
<td>-9.2</td>
<td>-7.8</td>
</tr>
<tr>
<td>HOClO</td>
<td>9.1</td>
<td>10.3</td>
<td>0.8</td>
<td>6.2</td>
</tr>
<tr>
<td>TS1</td>
<td>8.9</td>
<td>23.3</td>
<td>-6.4</td>
<td>3.7</td>
</tr>
<tr>
<td>TS2</td>
<td>7.4</td>
<td>46.6</td>
<td>29.8</td>
<td>39.0</td>
</tr>
<tr>
<td>TS3</td>
<td>7.4</td>
<td>26.8</td>
<td>18.7</td>
<td>19.3</td>
</tr>
<tr>
<td>TS4</td>
<td>9.8</td>
<td>54.2</td>
<td>50.6</td>
<td>33.6</td>
</tr>
<tr>
<td>TS5</td>
<td>8.4</td>
<td>15.5</td>
<td>11.2</td>
<td>-2.1</td>
</tr>
<tr>
<td>TS6</td>
<td>8.5</td>
<td>11.6</td>
<td>39.3</td>
<td>17.2</td>
</tr>
<tr>
<td>TS7</td>
<td>8.5</td>
<td>9.9</td>
<td>36.1</td>
<td>15.7</td>
</tr>
<tr>
<td>TS8</td>
<td>5.6</td>
<td>12.3</td>
<td>15.5</td>
<td>17.9</td>
</tr>
<tr>
<td>TS9</td>
<td>6.2</td>
<td>33.7</td>
<td>28.7</td>
<td>32.2</td>
</tr>
<tr>
<td>TS10</td>
<td>7.7</td>
<td>-12.1</td>
<td>-4.2</td>
<td>-3.8</td>
</tr>
<tr>
<td>TS11</td>
<td>8.2</td>
<td>23.9</td>
<td>38.9</td>
<td>26.6</td>
</tr>
<tr>
<td>HOO + Cl</td>
<td>8.9</td>
<td>-1.1</td>
<td>-5.7</td>
<td>-2.7</td>
</tr>
<tr>
<td>HCl + (^1)O(_2)</td>
<td>6.5</td>
<td>-16.3</td>
<td>-38.3</td>
<td>-30.2</td>
</tr>
<tr>
<td>HCl + (^3)O(_2)</td>
<td>6.6</td>
<td>-54.7</td>
<td>-68.6</td>
<td>-56.7</td>
</tr>
<tr>
<td>HOCl + (^3)O</td>
<td>8.3</td>
<td>13.2</td>
<td>4.1</td>
<td>10.0</td>
</tr>
</tbody>
</table>

\(^a\)The total energies of the reactants at different level are given in units of a.u and the relative energies of other species (to the reactants including ZPE corrections) at the corresponding levels are given in units of kcal/mol.

\(^b\)Values are given in units of kcal/mol
Table 2. Vibrational frequencies and moments of inertia for the reactants, intermediates, transition states and products of the OH (OD) + ClO reactions at the B3LYP/6-311+G(3df, 2p) level of theory.

<table>
<thead>
<tr>
<th>Species</th>
<th>I/a.u.</th>
<th>Frequencies/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>0.0, 3.2, 3.2</td>
<td>3722</td>
</tr>
<tr>
<td>OD</td>
<td>0.0, 6.0, 6.0</td>
<td>2717</td>
</tr>
<tr>
<td>ClO</td>
<td>0, 97.3, 97.3</td>
<td>861</td>
</tr>
<tr>
<td>HOOCl</td>
<td>35.6, 297.1, 326.7</td>
<td>375, 429, 640, 896, 1419, 3715</td>
</tr>
<tr>
<td>DOOC1</td>
<td>39.2, 311.9, 340.3</td>
<td>310, 381, 638.6, 895, 1052, 2715</td>
</tr>
<tr>
<td>HOCIO</td>
<td>51.7, 216.5, 262.6</td>
<td>329, 416.7, 622.6, 991.7, 1194.7, 3739.9</td>
</tr>
<tr>
<td>HClO₂</td>
<td>44.6, 182.4, 216.6</td>
<td>445, 976, 1045, 1045, 1146, 2200</td>
</tr>
<tr>
<td>Trans-³HOOCl</td>
<td>34.8, 472, 506.6</td>
<td>134, 225, 406, 1175, 1436, 3602</td>
</tr>
<tr>
<td>Cis-³HOOCl</td>
<td>45.9, 395, 441</td>
<td>207, 257.9, 636, 1206, 1440, 3345</td>
</tr>
<tr>
<td>³HOCIO</td>
<td>118.2, 275.4, 393.7</td>
<td>137, 174, 362, 740, 1301, 3668</td>
</tr>
<tr>
<td>TS1</td>
<td>84.9, 220.3, 305</td>
<td>487i, 308, 387, 903, 964, 3681</td>
</tr>
<tr>
<td>TS2</td>
<td>45.6, 204.9, 242.1</td>
<td>1601i, 349,705, 812,1053, 2284</td>
</tr>
<tr>
<td>TS3</td>
<td>34.9, 330.7, 360.2</td>
<td>1565i, 296, 477, 737, 863, 2834</td>
</tr>
<tr>
<td>TS4</td>
<td>75, 222, 291</td>
<td>785i, 476, 769, 836,1060, 3695</td>
</tr>
<tr>
<td>TS5</td>
<td>48.1, 394.1, 441.1</td>
<td>592i, 260, 549,1278, 1429, 2377</td>
</tr>
<tr>
<td>TS5 for (OD + ClO)</td>
<td>51.1, 398.1, 447.3</td>
<td>491i, 253, 465,1086, 1264, 1744</td>
</tr>
<tr>
<td>TS6</td>
<td>17.8, 440.8, 458.6</td>
<td>796i, 238, 393, 538, 1019, 3737</td>
</tr>
<tr>
<td>TS7</td>
<td>18.6, 441.5, 460.1</td>
<td>727i, 238, 429, 537,1017, 3741</td>
</tr>
<tr>
<td>TS8</td>
<td>53.5, 423.8, 476.8</td>
<td>1412i, 136, 451, 797, 1181, 1362</td>
</tr>
<tr>
<td>TS9</td>
<td>31.4, 545.2, 576.5</td>
<td>2140i, 101, 180, 304, 1068, 2686</td>
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<tr>
<td>TS10</td>
<td>49.1, 404.6, 453.7</td>
<td>639i, 197, 824, 971, 1296, 2098</td>
</tr>
<tr>
<td>TS11</td>
<td>17.8, 440.8, 458.6</td>
<td>781i, 127, 225, 423, 1167, 3777</td>
</tr>
<tr>
<td>HOO</td>
<td>2.9, 53.2, 56.1</td>
<td>1171, 1442, 3614</td>
</tr>
<tr>
<td>DOO</td>
<td>5.3, 56.5, 61.7</td>
<td>1059, 1188, 2641</td>
</tr>
</tbody>
</table>
Table 3. Heats of formation (in kcal/mol) predicted at the G2M //B3LYP/6-311+G (3df, 2p) level.

<table>
<thead>
<tr>
<th>Species</th>
<th>Predicted</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>OClO</td>
<td>25.3</td>
<td>23.7 ± 1.9</td>
</tr>
<tr>
<td>ClOO</td>
<td>23.5</td>
<td>23.8 ± 0.7</td>
</tr>
<tr>
<td>HOCl</td>
<td>-16.0</td>
<td>-17.1 ± 0.5</td>
</tr>
<tr>
<td>HO₂</td>
<td>1.6</td>
<td>1.2 ± 2.0</td>
</tr>
</tbody>
</table>

*a. The heats of formation were evaluated on the basis of the predicted heats of reaction from OH + ClO to the various product pairs, H + OClO, H + ClOO, O + HOCl and HO₂ + Cl.

Table 4. Predicted individual, total rate constants and product branching ratio at 200 – 2500 K for the reactions of OH (OD) + ClO

<table>
<thead>
<tr>
<th>T (K)</th>
<th>k₂ᵃ</th>
<th>kᵣᵇ</th>
<th>k₂/kᵣ</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>13.6 (8.04)</td>
<td>1.84 (1.81)</td>
<td>0.074 (0.044)</td>
</tr>
<tr>
<td>298</td>
<td>9.53 (5.78)</td>
<td>1.31 (1.27)</td>
<td>0.073 (0.046)</td>
</tr>
<tr>
<td>400</td>
<td>5.97 (4.50)</td>
<td>0.99 (0.96)</td>
<td>0.073 (0.047)</td>
</tr>
<tr>
<td>500</td>
<td>5.89 (3.79)</td>
<td>0.81 (0.78)</td>
<td>0.074 (0.048)</td>
</tr>
<tr>
<td>1000</td>
<td>4.09 (2.84)</td>
<td>0.49 (0.47)</td>
<td>0.084 (0.061)</td>
</tr>
<tr>
<td>1500</td>
<td>4.24 (3.11)</td>
<td>0.43 (0.41)</td>
<td>0.099 (0.077)</td>
</tr>
<tr>
<td>2000</td>
<td>4.96 (3.74)</td>
<td>0.42 (0.40)</td>
<td>0.118 (0.094)</td>
</tr>
<tr>
<td>2500</td>
<td>5.95 (4.57)</td>
<td>0.43 (0.41)</td>
<td>0.137 (0.11)</td>
</tr>
</tbody>
</table>

ᵃValues are in units of 10⁻¹³ cm³ molecule⁻¹ s⁻¹; the values in the parenthesis are for the OD + ClO reaction.
ᵇValues are in units of 10⁻¹¹ cm³ molecule⁻¹ s⁻¹
Figures captions

Fig. 1. The optimized geometry of the reactants, intermediates and products computed at the B3LYP/6-311+G(3d, 2p) level for the OH + ClO reaction.

Fig. 2. The geometry of the transition states involved in the OH + ClO reaction at the B3LYP/6-311+G(3d, 2p) level.

Fig. 3. The schematic diagram of the singlet potential energy surface for the OH-ClO system computed at the G2M level. The values in the parenthesis corresponding to the OD + ClO reaction (only the values used for rate constant calculation are presented).

Fig. 4. The schematic diagram of the triplet potential energy surface for the OH-ClO system computed at the G2M level.

Fig. 5. Comparison of the predicted total rate constants with the experimental values. Thick dotted line is the predicted results based one the G2M energies; thick solid line is the predicted result using the best heat of formation for HO2; thick dash line is the predicted result for the formation of HCl + ¹O2. Symbols and symbols with lines are the experimental results as indicted in the following: ▼ ref. 3; — ○ — ref.4; — △ — , ref. 5; ♦ ref. 6; ----●---- ref. 7; ⊕ ref. 9; ◇ ref. 11; ▲ ref.12; ▼ ref.13(b); *--- ref. 18; ---×--- ref. 19.

Fig. 6. Comparison of the predicted and experimental results for the reactions of: (a) OH + ClO → HCl + ¹O2 ; (b) OD + ClO → DCl + ¹O2 . Dotted lines are the results based on the G2M PES; solid lines are based on the best heat of formation of HO2; symbols are the experimental values, ○ ref. 9; ▼ ref. 10; ●- ref. 12.
Fig. 1
H-O-Cl-O = 110.1, TS2
H-O-O-Cl = 101.6, TS3
H-O-O-Cl = 101.9, TS4
H-O-O-Cl = -22.5, TS5
HOOC1 = 0.0, TS6
HOOC1 = 0.0, TS7
Cl-O-H-O = 96.4, TS8
H-O-O-Cl = 180.0, TS9
H-O-O-Cl = 0.0, TS10
H-O-O-Cl=180.0, TS11

Fig. 2
Fig. 3

Singlet Surface

\[ \text{HClO}_2 \]

\[ \text{HO} + \text{ClO}_2 \]

\[ \text{HOO} + \text{Cl} \]

\[ \text{TS1} \quad 3.7 \]

\[ \text{TS2} \quad 39.0 \]

\[ \text{TS3} \quad 19.3 \]

\[ \text{TS4} \quad 33.6 \]

\[ \text{TS5} \quad -2.1 (-2.2) \]

\[ \text{HOOCl} \quad -35.6 (36.2) \]

\[ \text{HOCIO} \quad -28.6 \]

\[ \text{HOClO} \quad -28.6 \]

\[ \text{HCl} + ^1\text{O}_2 \quad -30.2 (-30.0) \]
Fig. 4
Fig. 5
Fig. 6

(a) OH + ClO

(b) OD + ClO