Decomposition and Isomerization of the CH_3CHClO Radical: ab Initio and RRKM Study

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Twelve unimolecular reaction channels of the CH_3CHClO radical have been studied using the ab initio G2(MP2,SVP) method. The calculations detailed three kinds of mechanisms, i.e., bond scission, intramolecular three-center elimination, and isomerization. On the basis of ab initio data, we performed multichannel (up to eight channels) RRKM calculation and numerical master equation analysis. The energy-specific rate constants, $k(E)$, and the thermal rate constants, $k(T,P)$, were obtained. The three-center elimination of HCl from CH_3CHClO was shown to be the dominant decomposition pathway. This finding provides theoretical evidence for the previous experimental result. The implication of our results was discussed in terms of understanding the atmospheric fate of the chemically activated or thermally balanced CH_3CHClO radicals.

I. Introduction

Halogenated alkoxy radicals have been of significant interest recently in atmospheric and combustion chemistry. In the lower atmosphere they are formed in the following manner.[1−8] Hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs), which have been widely used as chlorofluorocarbon (CFC) substitutes, react with OH radicals to produce halogenated alkyl radicals which then rapidly add molecular oxygen to form peroxy (RO_2) radicals. These species will subsequently react with NO to form the corresponding halogenated alkoxy radicals. It has been shown that the halogenated alkoxy radicals formed in this manner are highly vibrationally excited. These hot radicals play an important role not only in their atmospheric fates but also in the degradation mechanism of other organic compounds.[8,9] In addition, the self-reactions of peroxy radicals are also a possible source of halogenated alkoxy radicals.[1−3] However, these types of reactions are nearly thermoneutral and the born alkoxy radicals cannot be chemically activated. On the other hand, the halogenated alkoxy radicals are believed to be key intermediates in the incineration of hazardous chemical wastes under fuel-lean condition.[10−15] Evidently, the unimolecular decomposition and isomerization of the halogenated alkoxy radicals are of special significance under both the chemical activation and the high-temperature combustion conditions.

The 1-chloroethoxy radical (CH_3CHClO) is one of the most important halogenated alkoxy radicals. A few experimental studies of the decomposition of CH_3CHClO were carrier out at Ford Motor Co.[4−6] Unfortunately, all those experimentalists confined themselves to the study of intramolecular three-center HCl-elimination mechanism which was first proposed by Shi, Wallington, and Kaiser.[4] The major experimental findings are as follows: (i) Three-center elimination of HCl from CH_3CHClO may be the dominant channel, and other decomposition pathways are minor. (ii) At 295 K, the lower limit of the rate constant is about 5×10^5 or 2×10^6 s^{-1} for elimination of HCl. (iii) The reaction of CH_3CHClO with O_2 is slow compared to elimination of HCl. Although there is enough experimental evidence for these unusual results, no theoretical evidence is reported to date. Moreover, the previous experiments are far from satisfactory in understanding the overall unimolecular reaction mechanism of the CH_3CHClO radical. To explain the experimental results and to predict the new characteristics about the loss of CH_3CHClO, a theoretical investigation is most desirable.

Actuated by such a goal, we present a study of the decomposition and isomerization of the CH_3CHClO radical using ab initio molecular orbital (MO) theory and RRKM theory. Five issues were addressed in this work: (i) The overall reaction mechanism, including bond scission, three-center elimination, and isomerization. (ii) The features of potential energy surface at the high level of theory, including the barrier heights and heats of reaction. (iii) The energy-specific rate constants of various reaction channels. (iv) The macroscopically observable thermal rate constants of the multichannel reaction of CH_3CHClO and the falloff behavior. (v) The lifetime of CH_3CHClO in the troposphere. So far as we know, this is the first theoretical study concerning the reactions of halogenated ethoxy radicals.

II. Computations

Geometries of the reactants, products, and transition states were optimized using the unrestricted second-order Møller−Plesset perturbation theory with the standard 6-31G(d) basis set and all electrons included [UMP2(full)/6-31G(d)].[16] Each stationary point was characterized through normal-mode analysis at the same level of theory. The transition state has one imaginary frequency, and the minimum has no imaginary frequency. In addition, all transition states were subjected to internal reaction coordinate (IRC)[17] calculations to facilitate connection between the reactants and the products. Each IRC terminated after reaching a minimum in each side. Once all critical points were determined, the energies were refined at the G2(MP2,SVP) level[18] which is one of the variations of Gaussian-2 theory.[19] For the present large system involving four heavy atoms, the G2(MP2,SVP) theory appears to be more effective than other methods in the calculation of molecular energies in view of computational accuracy and cost. It has been shown that this method performs well for hydrocarbons and radicals with an average absolute deviation of less than 2 kcal/mol from experiment.[20,21] Note that these refined energies were

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corrected for zero-point energies (ZPE) using the UMP2(full)/6-31G(d) frequencies which have been scaled by a factor of 0.93 to partly eliminate the known systematic errors.[22]

The energy-specific rate constants, $k(E)$, of different reaction channels were evaluated by Rice−Ramsperger−Kassel−Marcus (RRKM) theory using a simple treatment of adiabatic rotations. Subsequently, these data were utilized to calculate the thermal rate constants, $k(T,P)$, at various temperatures and pressures through solving the master equation numerically. The basic procedure used has been described in detail previously[23] and will not be detailed here.

The ab initio calculations were performed using the Gaussian 94 programs.[24] The RRKM calculations were carried out using the UNIMOL program package on the basis of ab initio data.[25]

III. Results and Discussion

A total of 12 unimolecular reaction pathways were examined in this study, viz.:

$$CH_3CHClO \rightarrow Cl + CH_3CHO \tag{1}$$

$$\rightarrow H + CH_3CClO \tag{2}$$

$$\rightarrow CH_3 + CHClO \tag{3}$$

$$\rightarrow HCl + CH_3CO \tag{4}$$

$$\rightarrow HCO + CH_3Cl \tag{5}$$

$$\rightarrow ClCO + CH_4 \tag{6}$$

$$\rightarrow CH_3CCl(OH) \tag{7}$$

$$\rightarrow CH_2CHCl(OH) \tag{8}$$

$$CH_3CCl(OH) \rightarrow CH_2CHCl(OH) \tag{9}$$

$$\rightarrow H + CH_3CClO \tag{10}$$

$$\rightarrow HCl + CH_3CO \tag{11}$$

$$CH_2CHCl(OH) \rightarrow OH + CH_2CHCl \tag{12}$$

where reactions 1−3, 4−6, and 7−8 correspond to the bond scission, three-center elimination, and isomerization of CH_3CHClO, respectively. Reactions 9−11 are the isomerization and decomposition of the isomer $CH_3CCl(OH)$, and reaction 12 is the CO bond cleavage of the other isomer $CH_2CHCl(OH)$. The geometries of the reactants, products, and transition states are shown in Figure 1. The vibrational frequencies are listed in the Supporting Information. The barrier heights and heats of reaction for reactions 1−12 are presented in Table 1. We have used simple abbreviated names for the transition states (TS), that is to say, TS*i* stands for the transition state for the reaction *i*. Note that reaction 12 is barrierless.

It is worth clarifying two issues before discussion. First, we did not constrain symmetry of the system in the optimization. As a matter of fact, all the reactants and transition states do not have symmetry except TS11. In view of the overall electronic states of the products, the potential surface studied has the $^2A'$ asymptote. Second, the major problem in the application of unrestricted spin formalisms is that of contamination with higher spin states. The severe spin contamination could lead to a deteriorated estimation of the barrier height. As shown in Table 1, the expectation values of S^2 for the UHF zero-order wave functions range from 0.91 to 0.76 before annihilation. After annihilation, $\langle S^2 \rangle$ is 0.75 (the correct value for doublets). This suggests that the wave function is not strongly contaminated by states of higher multiplicity.

TABLE 1: Activation Energies (E_a) and Heats of Reactions (ΔH°_0) through Reactions 1−12

reactions	$\langle S^2 \rangle^a$	E_a (kcal/mol)^b	ΔH°_0 (kcal/mol)^b
1	0.91	8.2	2.5
2	0.88	15.6	4.8
3	0.87	12.2	2.3
4	0.90	7.4	−12.3
5	0.86	46.8	2.3
6	0.79	53.0	−10.6
7	0.80	26.8	−12.1
8	0.80	30.4	−3.8
9	0.81	48.2	8.3
10	0.91	31.5	16.9
11	0.77	34.7	0.2
12[c]	n/a	n/a	29.5

[a] The expectation values of S^2 before projection for the TS*i*. For the reactants, the values of $\langle S^2 \rangle$ are CH_3CHClO 0.76; $CH_3CCl(OH)$ 0.76; $CH_2CHCl(OH)$ 0.76. The $\langle S^2 \rangle$ of HBC is 0.76. After projection, $\langle S^2 \rangle$ is 0.75. [b] All the energies are calculated at the G2(MP2,SVP) level. The total energies (in hartrees) of the reactants are CH_3CHClO −613.24350; $CH_3CCl(OH)$ −613.26283; $CH_2CHCl(OH)$ −613.24962. The total energy of HBC in reaction 4 is −613.26674 hartrees. [c] Reaction 12 is a barrierless CO bond scission. n/a: not available.

1. Reaction Mechanism. The equilibrium structure of the CH_3CHClO radical is staggered. The OC bond is trans with respect to one of the CH bonds of the methyl group, and the OCCH structure is almost planar. The unpaired electron is located on oxygen atom, as indicated by the long CO single bond. The enthalpy of formation at 298 K of CH_3CHClO was calculated to be −17.8 kcal/mol at the G2(MP2,SVP) level. This value is in agreement with the experimentally estimated value of −18.9 kcal/mol.[4] The eclipsed structure of CH_3CHClO (the CO bond is cis with respect to one of the CH bonds of the methyl group) was shown to be a first-order top with an imaginary vibrational frequency of 241 cm^{-1} which originates from the internal rotation of the methyl group around CC axis. The energy of the eclipsed structure is about 3.0 kcal/mol higher than that of the staggered structure.

A. Bond Scission Mechanism. As mentioned above, reactions 1, 2, and 3 correspond to the CCl, CH, and CC bond scissions from the α-C of CH_3CHClO, respectively. It is interesting to note that all the three simple bond cleavage reactions involve well-defined transition states, i.e., TS1, TS2, and TS3. There are two structural characteristics for the three transition states. First, the breaking CCl, CH, and CC bonds are elongated by 18%, 38%, and 31%, respectively. So these transition states have rather late characters, as could be anticipated from the reaction endothermicity. Second, the CO bonds are shortened by 0.092, 0.154, and 0.156 Å, respectively. The short CO bond suggests double bond character. The calculations reveal that reactions 1, 2, and 3 have the medium energy barriers, i.e., 8.2, 15.6, and 12.2 kcal/mol at the G2(MP2, SVP) level, respectively. Evidently, the CCl bond scission appears to be the most favorable reaction pathway.

B. Three-Center Elimination Mechanism. Reactions 4, 5, and 6 correspond to three-center elimination of HCl, CH_3Cl, and CH_4 from the CH_3CHClO radical. These three decomposition reactions are quite intriguing as shown below.

Reaction 4 is the only decomposition channel which has been studied experimentally. The transition state, TS4, for this three-center pathway has been located. In TS4, the breaking CCl bond is stretched by 0.314 Å. The CH bond is stretched by only 0.051 Å, which is about 5% of the CH bond distance in the CH_3CHClO radical. Simultaneously, the ClCH angle decreases to

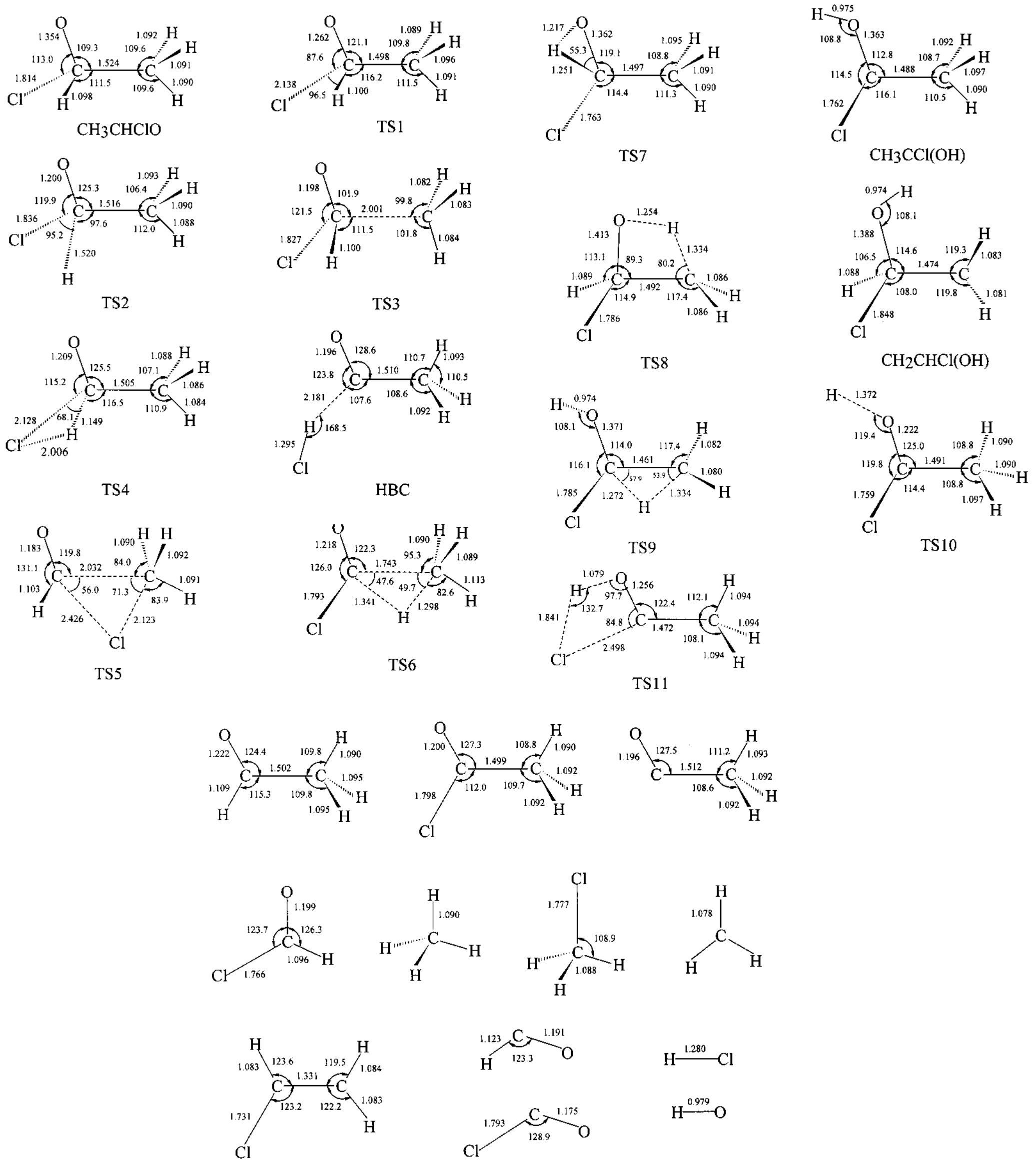

Figure 1. Theoretical geometrical parameters for the reactants, transition states, and products for reactions 1−12. Bond distances are in angströms and bond angles are in degrees.

68.1°. The forming HCl bond is 2.006 Å, which is 0.726 Å longer than the bond distance of the free HCl molecule. However, the geometric parameters of the other fragment, CH_3CO, are nearly the same as those of the CH_3CO radical. In light of these geometrical characteristics and the reaction exothermicity of 12.3 kcal/mol, it can be concluded that the HCl molecule may be born with vibrational excitation. The barrier height is 7.4 kcal/mol at the G2(MP2,SVP) level. This value is about 0.8 kcal/mol lower than that of TS1 and 8.2 kcal/mol lower than that of TS2. In addition, TS4 has an extremely large imaginary frequency, 2252 cm^{-1}. It implies that the quantum tunneling may play a significant role in reaction 4. Our calculation provides theoretical evidence for the existence of the three-center elimination of HCl from the CH_3CHClO radical. The IRC calculation reveals that there is a shallow well corresponding to a hydrogen-bonded complex (HBC) along the reaction's path. The hydrogen bonding occurs between the hydrogen of HCl and the carbonyl carbon (radical center) of CH_3CO. This HBC has C_s symmetry and $^2A'$ state. The hydrogen bond distance (C···H) is 2.181 Å, and the C···H···Cl structure is bent to 168.5°. The binding energy (D_0) is about 2.3 kcal/mol at the G2(MP2,SVP) level.

It is worth comparing the HCl elimination from CH_3CHClO with that from CH_2ClO. It has been shown that the CH_2ClO radical can also eliminate HCl through three-center pathway.[1−3,12,13] The geometric parameters of the transition state involved are very similar to those of the present TS4. The energy barrier for the HCl elimination from CH_2ClO was determined to be 10.9 kcal/mol at the G2(MP2) level, which is 3.5 kcal/mol higher than the barrier height of TS4. Therefore, the elimination of HCl from CH_3CHClO is easier than that from CH_2ClO. However, the three-center elimination of HCl from whether CH_2ClO or CH_3CHClO possesses the lowest energy barrier. As shown by the kinetic calculation later, this kind of pathway is the dominant decomposition channel. Since it has been found that other α-chlorinated alkoxy radicals can also eliminate HCl via the three-center mechanism,[7,13] this kind of intramolecular elimination of HCl appears to be typical for the loss of these radicals.

Very surprisingly, other two three-center elimination reactions 5 and 6 possess the quite high energy barriers, i.e., 46.8 and 53.0 kcal/mol at the G2(MP2,SVP) level, even though reaction 6 is exothermic. The high barriers prevent these two decomposition channels from proceeding to any extent. The structures of

TS5 and TS6 have been shown in Figure 1. In each of them, the synchronously breaking two bonds are elongated equally. The forming CCl bond in TS5 is about 29% longer than that in the CH_3Cl molecule. For the case of the forming CH bond in TS6, it is 19% longer than that in the CH_4 molecule.

C. Isomerization Mechanism. Two rearrangement pathways of the CH_3CHClO radical are conceivable. One of them is the 1,2-hydrogen shift from α-C to the terminal oxygen, forming the $CH_3CCl(OH)$ radical via the transition state TS7. The other is 1,4-hydrogen shift from β-C to the terminal oxygen, forming the $CH_2CHCl(OH)$ radical via the transition state TS8. Both $CH_3CCl(OH)$ and $CH_2CHCl(OH)$ are lower in energy than CH_3CHClO. The exothermicities of reactions 7 and 8 are 12.1 and 3.8 kcal/mol, respectively. The enthalpies of formation at 298 K for these two new isomers were also calculated at the G2(MP2,SVP) level, −29.7 kcal/mol for $CH_3CCl(OH)$ and −21.3 kcal/mol for $CH_2CHCl(OH)$. Compared with the geometry of the CH_3CHClO radical, both $CH_3CCl(OH)$ and $CH_2CHCl(OH)$ have the shorter CC bonds and the longer CO bonds. During the hydrogen shift, the radical center is moved in the opposite direction, from O to α-C in (7) and from O to β-C in (8). High energy barriers are involved in both reactions. The barrier heights are 36.8 and 32.0 kcal/mol at the G2(MP2,SVP) level for (7) and (8), respectively.

In principle, the CH_3CHClO radical can eliminate HCl or H_2 to form CH_2CHO or CH_2CClO through the four-center mechanism. We tried to locate the corresponding transition state but all our attempts failed. However, we can judge tentatively that the four-center mechanism may be unimportant in the decomposition of CH_3CHClO. Note that the four-center pathway is symmetry-forbidden because the products $HCl(^1\Sigma^+) + CH_2CHO(^2A'')$ or $H_2(^1\Sigma_g{}^+) + CH_2CClO(^2A'')$ at infinite separation have $^2A''$ electronic state. If the symmetry breaks, the reaction may occur. However, it must possess the high barrier because the β-CH bond is much stronger than the α-CH bond. This conjecture has been verified in the study of decomposition of CH_3CHFO.[26] We indeed found a transition state for the four-center HF elimination from CH_3CHFO. The corresponding barrier height was calculated to be 51.2 kcal/mol at the G2(MP2,SVP) level, which is much higher than the other energy barriers. Therefore, the four-center elimination from the analogous CH_3CHClO radical should have the similar energetics. As a matter of fact, the experimental study has demonstrated that the three-center elimination of HCl accounts for 85%−100% of the overall yield of HCl molecule.[5]

D. Decomposition of $CH_3CCl(OH)$ and $CH_2CHCl(OH)$. For completeness, we have also examined several unimolecular dissociation pathways of $CH_3CCl(OH)$ and $CH_2CHCl(OH)$, i.e., reactions 9−12. The structure TS9 is the transition state connecting these two isomers. It is a three-member ring structure. The migrating hydrogen atom departs from the two carbon atoms in the similar distance. The barrier height is 48.2 kcal/mol at the G2(MP2,SVP) level for this reorganization. Reaction 10 is the OH bond cleavage path with the formation of atomic hydrogen and acetyl chloride. This reaction is endothermic by 16.9 kcal/mol. The transition state TS10 has a rather late character as indicated by the elongated OH bond (by 41%). The corresponding energy barrier is rather high, 31.5 kcal/mol at the G2(MP2,SVP) level. The $CH_3CCl(OH)$ radical can also eliminate HCl to form CH_3CO, however, via the four-center transition state TS11. It is interesting to note that TS11 has C_s symmetry and $^2A'$ electronic state. The CCl bond is stretched significantly while the OH bond is stretched by only about 0.1 Å. The length of the forming HCl bond is much longer than that of the free HCl molecule. Reaction 11 is nearly thermoneutral. The barrier height is 34.7 kcal/mol at the G2(MP2,SVP) level. It is worth noting that the energy of the four-center TS11 is about 15.2 kcal/mol higher than that of the three-center TS4. Reaction 12 is the CO bond cleavage of $CH_2CHCl(OH)$ with the formation of OH and CH_2CHCl. This pathway was found to be barrierless, in accordance with the experimentally observed zero or negative activation energy for the reverse reaction.[27] The endothermicity of reaction 12 is 29.5 kcal/mol.

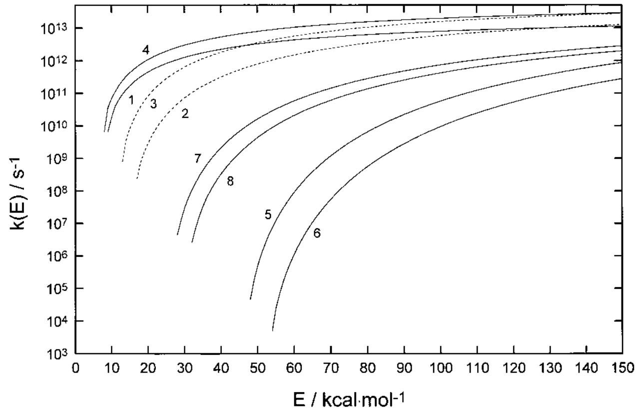

Figure 2. Microscopic rate constants for the unimolecular reactions 1−8 of the CH_3CHClO radical.

2. Reaction Kinetics. On the basis of ab initio frequencies, moments of inertia, and barrier heights, we performed RRKM calculation to determine the microscopic and thermal unimolecular rate constants of CH_3CHClO. Given an accurate treatment, the reverse processes of the isomerization reactions 7−8 and the decomposition reactions (9−12) of the two isomers should be taken into account. However, all these pathways appear to be unimportant because they have to surmount high energy barriers. For the purpose of simplification, they were omitted in the RRKM calculations. The UNIMOL program package[25] was used to carry out the kinetic calculations.

A. Microscopic Rate Constants. Figure 2 shows the microscopic rate constants of various reaction channels as a function of the internal energy E. Because reaction 4 involves the lowest activation barrier, it has the fastest rate over the whole energy range considered, which implies that reaction 4 may dominate the decomposition of CH_3CHClO. At lower energies, the rates of the three bond scission channels ((1)−(3)) have the ordering of $k_1(E) > k_3(E) > k_2(E)$, in accordance with the ordering of energy barriers. At energies greater than 48 kcal/mol, $k_3(E)$ exceeds $k_1(E)$. This is caused by the fact that the low frequencies of TS3 are generally smaller than those of TS1, leading to the larger sum of states for TS3. Moreover, $k_3(E)$ is close to $k_4(E)$ at higher energies. For the same reason, $k_2(E)$ exceeds $k_1(E)$ at energies greater than 133 kcal/mol. The rate constants of reactions 5−8 are apparently smaller than those of reactions 1−4. So the pathways 5−8 may play minor or negligible roles to the loss of CH_3CHClO.

B. Thermal Rate Constants. In contrast to microscopic condition, the macroscopically measurable thermal rate constants of the multichannel reactions of CH_3CHClO are interdependent.[23] Quantitative determination of the rate constants requires the solution to the master equation. Because of the numerical difficulty in such a solution, the unimolecular rate constants could be evaluated reliably only in the temperature range 250−500 K. The quantum tunneling correction has been estimated using the simple Wigner method,[28] i.e., $\kappa = 1 - (1/24)(h\nu_i/k_BT)^2\,(1 + k_BT/E_a)$, where ν_i is the imaginary frequency of TSi,

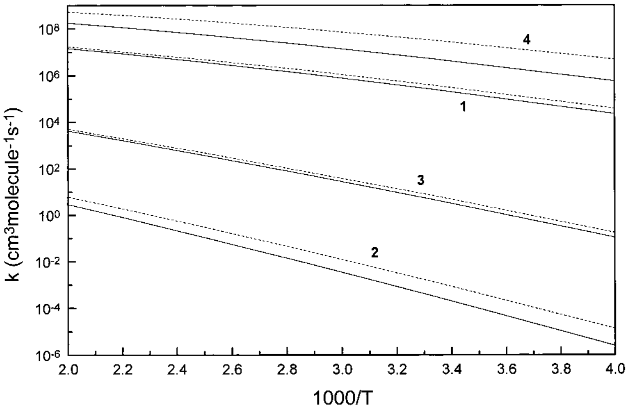

Figure 3. Arrhenius plot of the unimolecular rate constants of decomposition of CH_3CHClO at 760 Torr of N_2. Only the rate constants of reactions 1−4 are shown. The short-dashed lines show the rate constants with tunneling corrections.

E_a is the barrier height, k_B is the Boltzmann constant, and h is the Planck constant. During the calculation, we found that the thermal rate constants of reactions 5−8 are far smaller than those of reactions 1−4 (by more than 10 orders of magnitude). Consequently, we have confined ourselves to reactions 1−4 in the following discussion.

First, RRKM calculations were performed for atmospheric pressure (760 Torr) with N_2 as the bath gas. The Arrhenius plot for the rate constants of reactions 1−4, calculated in the 250−500 K temperature range with and without tunneling corrections, is shown in Figure 3. Evidently, the rate of reaction 4 is fastest. The rate of reaction 1 is about 1 order of magnitude lower than that of reaction 4. The rates of reactions 2 and 3 are both much lower than those of reactions 4 and 1. So it can be concluded that reaction 4, i.e., the three-center elimination of HCl, does dominate the decomposition of CH_3CHClO. Being evidence for the reliability of this conclusion, it is noteworthy that the calculated rate constant at 295 K (P = 100 Torr) for reaction 4, 7.1×10^5 s^{-1} (or 4.5×10^6 s^{-1} with tunneling correction), is in agreement with the experimentally estimated lower limit,[5] 5×10^5 s^{-1} or 2×10^6 s^{-1}. The individual rate constants were fitted by least squares to the following Arrhenius expressions in s^{-1} for 250−500 K and 760 Torr of N_2:

$$k_1(T) = 1.1 \times 10^{10} \exp(-3236/T)$$

$$k_2(T) = 4.0 \times 10^{6} \exp(-6995/T)$$

$$k_3(T) = 2.0 \times 10^{8} \exp(-5297/T)$$

$$k_4(T) = 6.5 \times 10^{10} \exp(-2869/T)$$

without tunneling correction.

$$k_1(T) = 9.2 \times 10^{9} \exp(-3055/T)$$

$$k_2(T) = 3.4 \times 10^{6} \exp(-6528/T)$$

$$k_3(T) = 1.7 \times 10^{8} \exp(-5142/T)$$

$$k_4(T) = 7.0 \times 10^{10} \exp(-2344/T)$$

with tunneling correction.

We have also presented the falloff data for the unimolecular decomposition of CH_3CHClO at 300 K in Figure 4. The rate constant of the fastest reaction 4 approaches the high-pressure limit near 10^5 Torr. At atmospheric pressure and the lower pressures of the troposphere, it can be conceivable that the rates of all channels are in the falloff regimes.

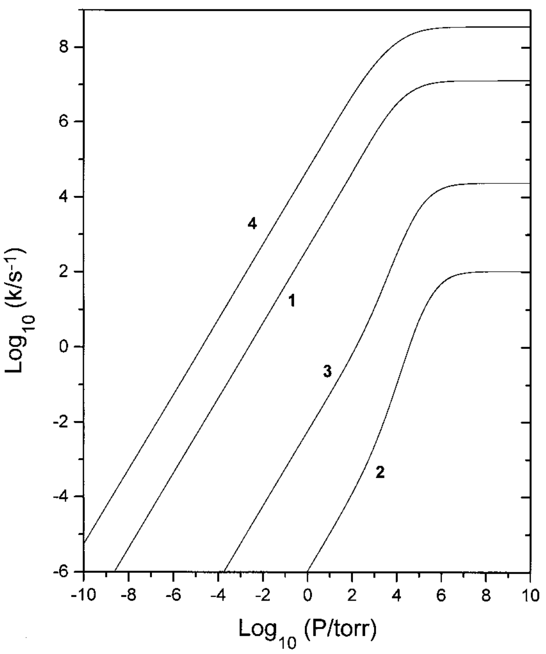

Figure 4. Falloff plot of the rate constants for reactions 1−4 at 300 K with N_2 as the bath gas.

It should be reminded that the calculated rate constants easily have 50% or larger uncertainty in view of various possible sources of error inherent in the present calculations (e.g., barrier height, anharmonic effect, etc.). Note that the difference between the barriers of reactions 1 and 4 is only 0.8 kcal/mol. If the G2(MP2,SVP) predicted barrier height on UMP2(full)/6-31G(d) geometry has a likely error of, at worst, greater than 2 kcal/mol, the CCl bond scission (reaction 1) may compete with the HCl elimination (reaction 4). However, both experiments and calculations tend to rule out this possibility.

C. Implication for Atmospheric Chemistry. The reactions of halogenated alkoxy radicals are of special importance in the troposphere.[1−8] Our calculations support the proposal that decomposition via intramolecular elimination of HCl is the dominant atmospheric fate of CH_3CHClO radicals.[4−6] At the present time we can estimate the lifetime of CH_3CHClO. As mentioned in the Introduction, the CH_3CHClO radicals can be formed through two paths, viz.:

$$CH_3CHClO_2 + NO \rightarrow CH_3CHClO + NO_2 \qquad (13)$$

$$CH_3CHClO_2 + CH_3CHClO_2 \rightarrow CH_3CHClO + CH_3CHClO + O_2 \qquad (14)$$

The heats of these two reactions were calculated to be −13.6 and 0.0 kcal/mol, respectively.[29] Reaction 13 is significantly exothermic and reaction 14 is thermoneutral. So the CH_3CHClO radicals formed through path 13 can be highly chemically activated. In case the excess energy is released entirely into the CH_3CHClO radical, the corresponding lifetime of the "hot" CH_3CHClO radical in the collision-free environment was estimated to be 2.4 ps using the energy-specific rate constant in Figure 2. On the other hand, the CH_3CHClO radicals formed in reaction 14 are cold. Under the typical tropospheric condition ($T \sim 230$ K and $P \sim 100$ Torr), the total rate of decomposition of CH_3-

CHClO is 3×10^5 s^{-1}. So the lifetime of the "cold" CH_3CHClO radical (or that formed in (13) but deactivated by bath gas) is about 3.3 μs. But again there is a significant uncertainty in this estimation.

IV. Concluding Remarks

Bond scission, intramolecular elimination, and isomerization pathways of unimolecular reaction of CH_3CHClO were fully detailed at the G2(MP2,SVP) level of theory. The reaction kinetics were studied using the RRKM theory with the solution of the master equation. The following findings in this investigation may be reasonable:

(i) The reaction mechanism involving the three-center elimination of HCl is the most favorable for the CH_3CHClO radical decomposition. The critical transition state for this channel, TS4, lies 7.4 kcal/mol above CH_3CHClO. This result provides theoretical evidence for the previously experimental proposal.

(ii) The calculated unimolecular rate constants exhibit Arrhenius behavior in the temperature range of 250−500 K. At 300 K, the high-pressure limit of rate constant occurs near 10^5 Torr. Under the atmospheric condition, the unimolecular rate constants are in the falloff regimes.

(iii) The CH_3CHClO radicals can have two kinds of lifetimes in the troposphere. For the vibrationally excited CH_3CHClO, the lifetime is in the magnitude of picoseconds. For the cold CH_3CHClO, the lifetime may be in the magnitude of microseconds. Note that this result is a qualitative estimation rather than a quantitative conclusion.

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Supporting Information Available: Table S1 lists the optimized **Z**-matrices of various species. Table S2 lists the vibrational frequencies and moments of inertia of various species. Table S3 gives the thermal rate constants for channels 1−4, 7, and 8 at the selected temperatures and pressures. Figure S1 shows the geometrical parameters of the structures of interest other than those in the text. Figure S2 shows the IRC profile for the $CH_3CHClO \rightarrow HCl + CH_3CO$ reaction. Notes S1 and S2 detail the G2(MP2,SVP) method and the UNIMOL program, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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