

Theoretical Study of the Unimolecular Decomposition Mechanism of Chloromethanol

WANG, Shao-Kun*(王少坤) ZHANG, Qing-Zhu(张庆竹) HOU, Hua(侯华)

WANG, Bin(汪冰) LIU, Fu-Xiang(刘福祥) GU, Yue-Shu(顾月姝)

School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong 250100, China

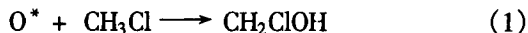
The decomposition pathways of chloromethanol have been studied by *ab initio* calculation. Equilibria and transition states have been optimized at the UMP2(full)/6-31G(d) level. The single point energies have been obtained at higher level of G3(MP2). Four transition states and eight reaction pathways have been revealed and the most favorable reaction to decomposition pathway is the 1,2-HCl elimination, which is consistent with the former scientist's conclusion.

Keywords *Ab initio*, decomposition, reaction mechanism, chloromethanol

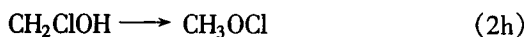
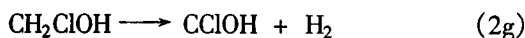
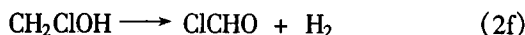
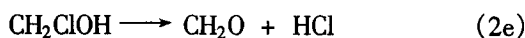
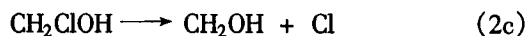
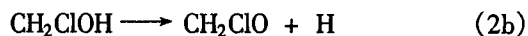
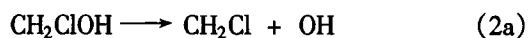
Introduction

Chemical dynamics of the reactions of $O^*(^1D)$ with halogenated hydrocarbons¹⁻³ have been of considerable interest in recent years, due to their importance in both atmosphere and combustion.

Electronic excited oxygen $O^*(^1D)$ can insert CH bond in CH_3Cl and produce vibrationally excited monochloromethanol (CH_2ClOH).



A few products can be formed from such an intermediate as follows Eq. (2):



In order to understand the reaction mechanisms of these product channels and the role of vibrationally excited CH_2ClOH in the atmosphere, we use *ab initio* calculations to predict the respective heat of reaction and activation energy.

Computation method

All calculations were performed using the Gaussian 94 program,⁴ and the polarized split-valence 6-31G(d) basis sets. Geometry optimization were carried out for all equilibria and transition states at the second-order unrestricted second-order Møller-Plesset perturbation level (MP2) of theory. Intrinsic reaction coordinate (IRC) calculations prove that the transition states link the designed products and reactant. Harmonic vibration frequencies and zero-point energies for the reactions, the products and the transition states were calculated analytically at the same level of theory. The single energies of all species were calculated at the G3(MP2) theoretical level.

G3(MP2) theory is based on MP2(full)/6-31g(d) geometries. A series of single point energy calculations were carried out at higher levels of theory. The subsequent calculations include only valence electrons in the

* E-mail: guojz@icm.sdu.edu.cn.

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treatment of electron correlation, *i. e.*, frozen core (fc). The first higher level calculation is at the quadratic configuration interaction level of theory⁵ with the 6-

31G(d) basis set, *i. e.* QCISD(T)/6-31G(d), this energy is then modified by a series of corrections to obtain a total energy E_0 :

$$E_0[\text{G3(MP2)}] = \text{QCISD(T)/6-31G(d)} + \Delta E_{\text{MP2}} + \Delta E(\text{SO}) + E(\text{HLC}) + E(\text{ZPE}) \quad (3)$$

The correction at the second-order Møller-Plesset level (MP2) is given by

$$\Delta E_{\text{MP2}} = [E(\text{MP2/G3MP2large})] - [E(\text{MP2/6-31G(d)})] \quad (4)$$

The other corrections in Eq. (3) are similar to those in G3 theory.⁶

Results and discussion

Fig. 1 shows the optimized geometries for all species at the UMP2(full)/6-31G(d) level. The har-

monic vibration frequencies at UMP2(full)/6-31g(d) level for all species are presented in Table 1. Total and relative energies for all the stationary points, computed at G3(MP2) level, are given in Table 2. Energetic profile for the decomposition of monochloromethanol is shown in Fig. 2. The most possible reaction pathway's IRC is shown in Fig. 3.

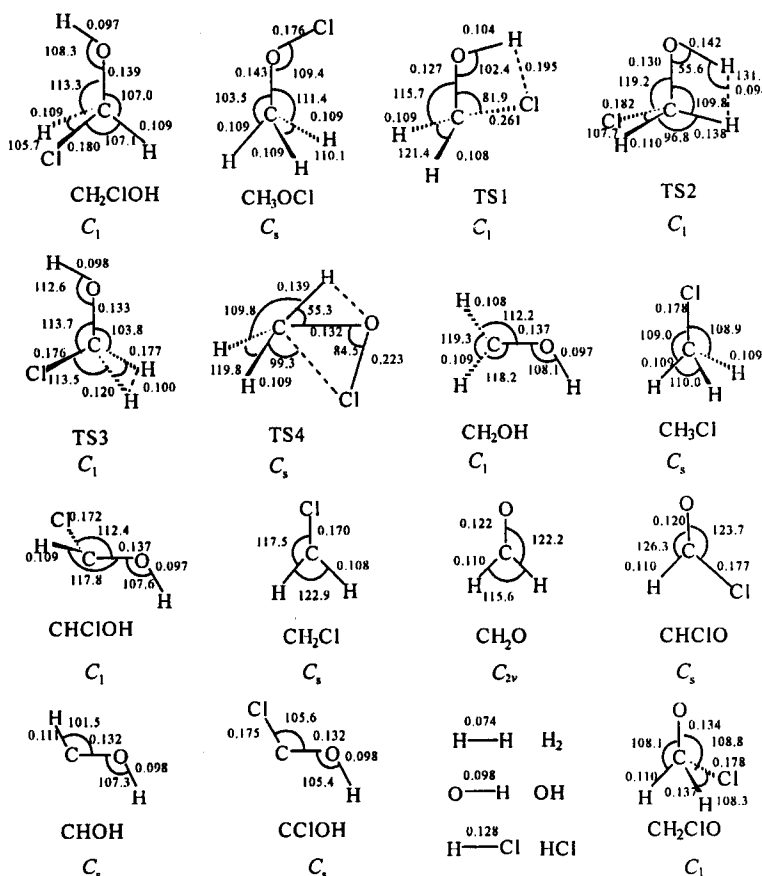


Fig. 1 Optimized geometries of the various stationary points at the UMP2(full)/6-31G(d) level. Bond lengths are in nm and bond angles are in degree.

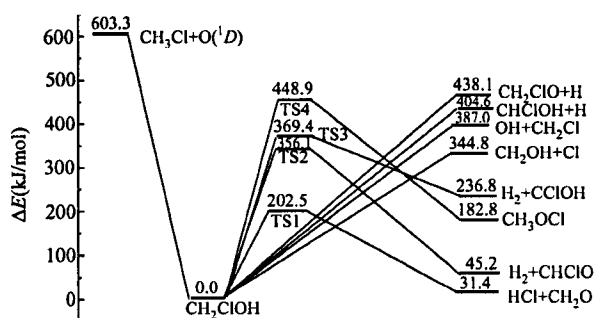


Fig. 2 Energetic profile (kJ/mol) for the decomposition of monochloromethanol.

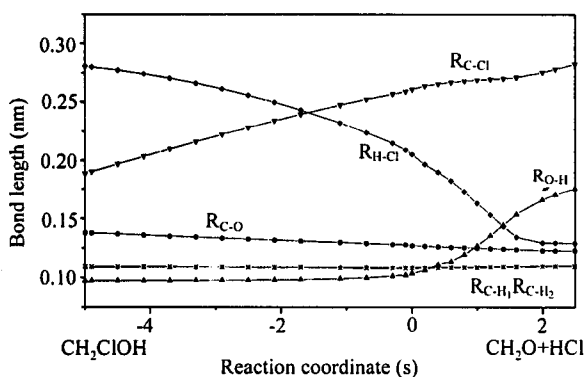


Fig. 3 Most possible reaction pathway's IRC ($\text{CH}_2\text{ClOH} \longrightarrow \text{CH}_2\text{O} + \text{HCl}$).

Table 1 Vibrational frequencies (cm^{-1}) and zero-point energies (ZPE, kJ/mol) for various species involved in the CH_2ClOH system

Species	Frequencies	ZPE
CH_3Cl	731, 1010, 1010, 1366, 1439, 1439, 2930, 3035, 3035	102.9
CH_2ClOH	339, 428, 684, 936, 1061, 1156, 1312, 1348, 1455, 2928, 3029, 3501	108.8
CH_3OCl	250, 351, 655, 984, 1116, 1137, 1403, 1426, 1460, 2884, 2970, 3000	105.4
TS1	600i ^a , 273, 532, 848, 994, 1111, 1325, 1376, 1534, 2576, 3006, 3150	100.0
TS2	2209i, 353, 595, 629, 901, 976, 1249, 1261, 1442, 1858, 2134, 2890	85.4
TS3	1343i, 405, 512, 578, 651, 730, 1136, 1220, 1260, 1378, 2225, 3378	80.8
TS4	1988i, 228, 406, 496, 622, 994, 1123, 1191, 1448, 1744, 2936, 3061	85.4
CHClOH	256, 388, 739, 825, 1141, 1170, 1321, 2981, 3503	73.6
CH_2OH	430, 728, 1021, 1145, 1306, 1440, 2977, 3120, 3533	93.7
CH_2ClO	382, 687, 698, 1043, 1054, 1287, 1339, 2870, 2932	73.6
CClOH	438, 691, 718, 1227, 1242, 3425	46.4
CHOH	1060, 1149, 1273, 1442, 2748, 3428	66.5
CHClO	437, 719, 905, 1307, 1685, 2930	47.7
CH_2O	1129, 1206, 1474, 1667, 2799, 2865	66.5
CH_2Cl	307, 822, 985, 1391, 3041, 3182	58.6

^ai represents imaginary frequency.

Table 2 G3(MP2) total energies (E_0 , Hartree) and the relative energies (ΔE , kJ/mol) for various species through the decomposition reactions of CH_2ClOH

Species	E_0 [G3(MP2)] ^a	ΔE ^a
CH_2ClOH	-574.71821	0.0
CH_3OCl	-574.64860	182.8
$\text{CH}_2\text{O} + \text{HCl}$	-574.70627	31.4
$\text{CH}_2\text{Cl} + \text{OH}$	-574.57089	387.0
$\text{CH}_2\text{OH} + \text{Cl}$	-574.58689	344.8
$\text{CHClOH} + \text{H}$	-574.56417	404.4
$\text{H}_2\text{ClO} + \text{H}$	-574.55135	438.1
$\text{CHClO} + \text{H}_2$	-574.70109	45.0
$\text{CClOH} + \text{H}_2$	-574.62808	236.6
$\text{O}(^1D) + \text{CH}_3\text{Cl}$	-574.48843	603.3
TS1	-574.65604	163.2
TS2	-574.58261	356.0
TS3	-574.57749	369.5
TS4	-574.54726	448.8

^aBoth E_0 [G3(MP2)] and ΔE have included the ZPE corrections. ΔE is the difference between the E_0 [G3(MP2)] of various species and the E_0 [G3(MP2)] of the CH_2ClOH molecule.

Product of $\text{O}(^1D)$ and CH_3Cl

As Fig. 2 shown, $\text{O}(^1D)$ and CH_3Cl can react, and produce abundant energetic CH_2ClOH . Compared with $\text{O}(^1D)$ and CH_3Cl , CH_2ClOH has 603.3 kJ/mol vibration energy, so it can make unimolecular decomposition, isomerization and bond fission reaction.

Bond fission mechanism

CH_2ClOH can produce bond scission. The CH , CCl , OH and CO bond cleavages of CH_2ClOH produce $\text{H} + \text{CHClOH}$, $\text{Cl} + \text{CH}_2\text{OH}$, $\text{H} + \text{CH}_2\text{ClO}$ and $\text{OH} + \text{CH}_2\text{Cl}$ respectively. They are the reverse processes of the "barrierless" radical-radical recombination reaction. At G3(MP2) level, the CH , CCl , OH and CO bond dissociation energies are 404.4, 344.8, 438.1, and 387.0 kJ/mol, respectively. So these fission reactions are difficult to occur.

Four-member-ring elimination mechanism

There are two four-center product channels in the decomposition of CH_2ClOH , forming $\text{HCl} + \text{CH}_2\text{O}$ and $\text{CHClO} + \text{H}_2$ *via* the transition states TS1 and TS2, respectively. In TS1, the CCl and OH bonds are elongated 0.081 nm and 0.006 nm, respectively. The forming HCl bond length is 0.195 nm, and is 0.067 nm longer than the equilibrium bond length of HCl. The HOC and ClCO angles are reduced to only 102.4° and 81.9° respectively. It can be seen from Table 2 that the TS1 is a true first-order saddle point with an imaginary frequency of 600i (scaled). The barrier of TS1 is 163.2 kJ/mol. IRC (Fig. 3) proves that TS1 links CH_2ClOH on one side and $\text{CH}_2\text{O} + \text{HCl}$ on other side. As Fig. 2 shown, $\text{CH}_2\text{O} + \text{HCl}$ channel possesses not only the lowest energy barrier, but also the lowest endothermicity (31.4 kJ/mol) in all decomposition channels of CH_2ClOH . Thus this channel is the easiest reaction pathway. Experimental scientists discover that CH_2ClOH can decay to give HCHO and HCl in darkness. Photolyzed CH_2ClOH in Ar matrices can give $\text{HCl} + \text{CO} + \text{H}_2^{7-9}$ (High energetic HCHO can decompose to $\text{CO} + \text{H}_2$). That proves experimental scientists also believed that it is most possible reaction pathway that CH_2ClOH produces $\text{HCHO} + \text{HCl}$. In TS2, the O—H and C—H bonds are elongated 0.044 nm and 0.028 nm, respectively. The length of forming H—H bond is 0.098 nm, which is 0.024 nm longer than the equilibrium distance of the H_2 molecule. The H—O—C and H—C—O angles are reduced to 55.6° and 109.8° , respectively. TS2 is also a true first-order saddle point with an imaginary frequency of 2209i (scaled). In thermodynamic, although this reaction channel endothermicity is not significant (45.0 kJ/mol), the barrier height of TS2 is 356.0 kJ/mol which is higher than that of TS1. Compared with TS1 channel, this reaction pathway is difficult to occur.

Three-member-ring elimination mechanism

CH_2ClOH can produce $\text{CClOH} + \text{H}_2$ *via* three-center transition state TS3. In TS3, one of C—H bonds is elongated by about 0.068 nm while the other C—H bond stretches only by about 0.011 nm. The H—H bond is 0.100 nm, which is 0.026 nm longer than the equilibrium distance of the H_2 molecule. H—C—H angle is reduced to only 32.6° . TS3 is a true first-order saddle point with an imaginary frequency of 1343i (scaled). The barrier of TS3 is 369.5 kJ/mol. The reaction is endothermic (236.6 kJ/mol). Compared with TS2 chan-

nel, this channel is more difficult to occur.

Isomerization reaction mechanism

CH_2ClOH can rearrange to CH_3OCl *via* the transition state TS4. The migration of the H atom from O to C is accompanied by the migration of the Cl atom from C to O. TS4 has C_s symmetry and a $^1A'$ state. TS4 is also a true first-order saddle point with an imaginary frequency of 1988i. The activation energy of this isomerization channel is quite high, 448.8 kJ/mol. It implies that CH_3OCl is kinetically stable with respect to CH_2ClOH . However, thermodynamically, CH_3OCl is 182.8 kJ/mol unstable with respect to CH_2ClOH . So this reaction is the most difficult to occur.

Conclusion

We have studied four different dissociation mechanism of monochloromethanol: the bond fission, four-member-ring elimination, three-member-ring elimination and isomerization. The 1,2-HCl elimination channel is relatively ready to occur with respect to other channels because its barrier is the lowest (163.2 kJ/mol). Moreover, the endothermicity of 1,2-HCl elimination channel is the smallest. As for the bond fission, H_2 elimination and isomerization, the heats of their reactions are greatly larger than the barrier of the 1,2-HCl elimination, so these reactions require higher energy and they are also unlikely to occur to significant extent.

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