Vibrational Mode Analysis for the Multichannel Reaction of CH$_3$Cl + OH

Fahimeh Shojaie and Maryam Dehestani*

The recently presented *ab initio* calculations for the reaction system of CH$_3$Cl + OH (Dehestani and Shojaie, Int J Quantum Chem, in press) are applied to the vibrational mode analysis. Extending previous work, we use the vibrational mode analysis to elucidate the relationships of the reactants, the transition state, the intermediates (IM), and the products. The extensive investigation shows that the reaction mechanism is reliable. © 2011 Wiley Periodicals, Inc.

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Introduction

In a previous work,[1] we investigated the mechanism and kinetics of CH$_3$Cl + OH reaction by using quantum chemical methods and multichannel RRKM theory calculations for the total and individual rate constants of various channels in the temperature range of 200–2000 K and at a pressure of 760 Torr. The work was concentrated mainly on the rate constant calculations and revealed that the major channel is hydrogen-abstraction mechanism. No attempt has been reported so far to derive the vibrational wave numbers and modes of the reactants, the transition state (TS), the intermediates, and the products (P) from *ab initio* molecular orbital calculations. The aim of the present study is to elucidate the relationships of the species involving the reaction by using the vibrational mode analysis. In the present work, the vibrational mode analysis has performed to examine the reliability of the previously reported reaction mechanism. The extensive investigation shows that the reaction mechanism is reliable.

Results and Discussion

We will refer to the results obtained in our previous study.[1] We use the optimized geometric parameters and frequencies of predicted by the *ab initio* calculations reported in the preceding article.[1] In Figure 1, we show the reactants, intermediates, TSs, and products involved in CH$_3$Cl + OH reaction with atoms numbering. Analyzing the changes in vibrational modes from reactant (R) to TS and from TS to products can help us to elucidate the direction of the reaction. Therefore, the reaction mechanism appears to be uncovered. Subsequently, the reaction will be explained by using vibrational modes and frequencies. One can not distinguish between the vibrational modes of a complicated compound, but they can be assigned to six normal modes, namely, the twist mode, the rock in plane mode, the rock out of plane mode, the bend in plane mode, the symmetric stretch (or stretch) mode, and the asymmetric stretch.[2–4] All vibrational frequencies involving the

CH$_3$Cl + OH system are assigned to these six normal modes frequencies.

All the species involving in the reaction are optimized to the C_1 point group, with the exception of CH$_3$Cl, CH$_2$Cl, CH$_3$, HOCl, H$_2$O, OH, and HCl belonging to the C_{3v}, C_{2v}, D_{3h}, C_s, C_{2v}, $C_{\infty v}$, and $C_{\infty v}$ point groups, respectively. All the IMs and TSs have a single electron. The oscillation frequencies and their vibrational modes assignment for the reactants, products, intermediates, and TSs are listed in Tables 1–5.

Vibrational mode analysis for IM2 formation

As illustrated in Ref. [1], the pathway of IM2 formation can be written as:

$$R \rightarrow TS1 \rightarrow IM1 \rightarrow TS2 \rightarrow IM2$$

As shown in Figure 1, the OH radical is getting closer to the carbon atom of the CH$_3$Cl molecule by TS1 to form IM1. In TS1, the low imaginary frequency may indicate a relatively low energy barrier, so it is not surprising that this barrier is 1.6 kcal/mol higher than the reactants at the G2MP2 method (see Figure 2 in Ref. [1]). The vibrational mode of imaginary frequency of TS1 denotes that the OH radical has not completely migrated to the carbon atom. Comparison of modes in Table 2 shows that the modes in TS1 can exist in IM1 with frequencies similar or near to each other, for example, modes CH$_3$ bend in plane, C—Cl stretch, and CH$_3$ twist. Thus, they have similar structures, but in IM1, the O—C bond is shortened to 0.34 Å (see Figure 1). The OH radical add and Cl radical abstract from the C atom of the CH$_3$Cl molecule via TS2, leading to IM2. For

F. Shojaie, M. Dehestani
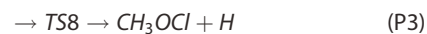*Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, Iran*
E-mail: dehestani@mail.uk.ac.ir
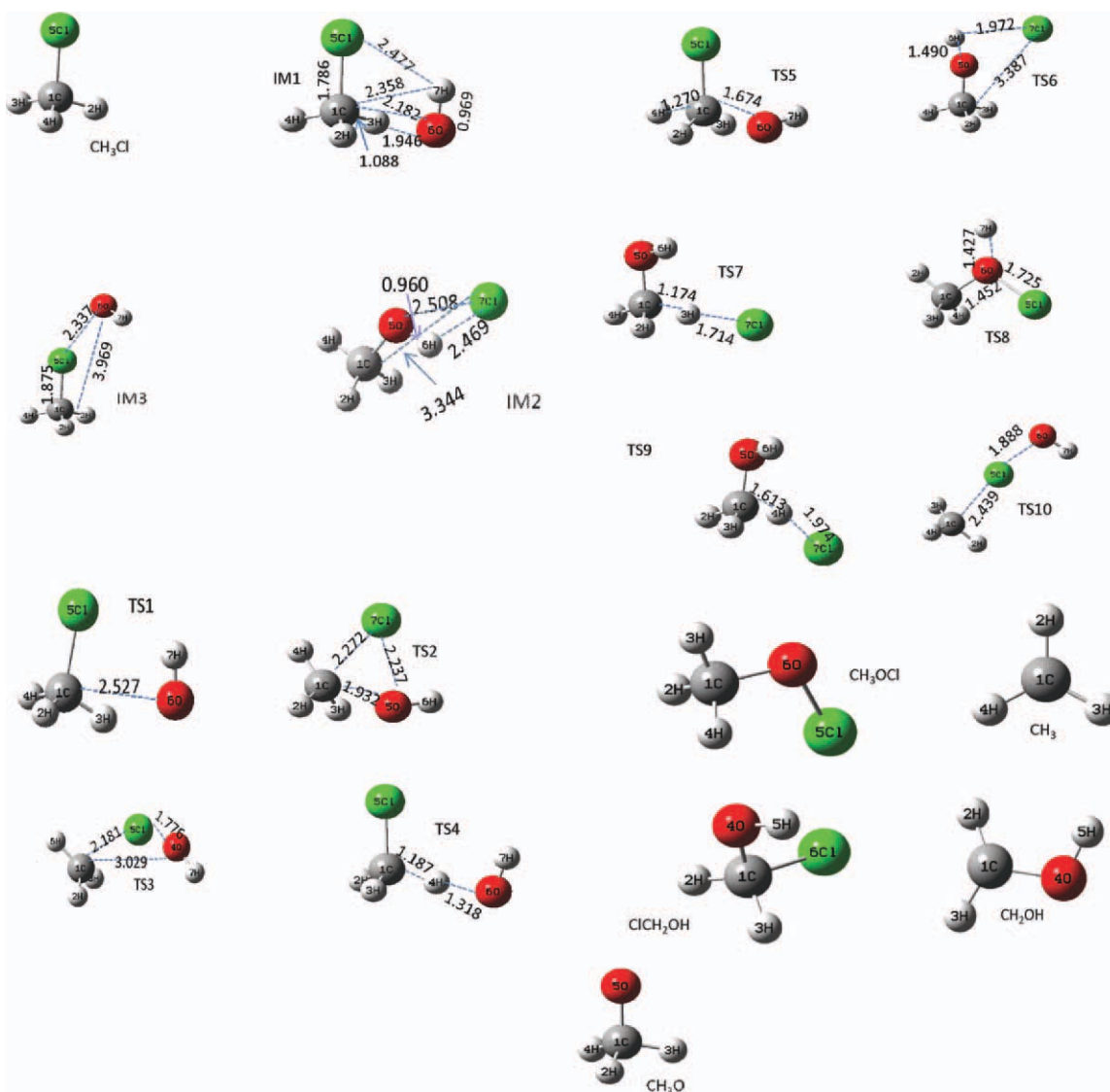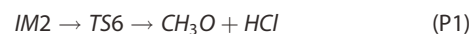
Figure 1. The reactant, intermediates, TSs and products involved in the $CH_3Cl + OH$ reaction with atoms numbering. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TS2, there are three stretch modes: one is the imaginary frequency (C—O stretch, i1075 cm^{-1}); the other two are Cl—C—O (453 cm^{-1}) and O—H6 (3823 cm^{-1}). These modes show that the OH radical has completely migrated to the carbon atom. Also C—O stretch mode at i1075 cm^{-1} of TS2 is increased to 1063 cm^{-1} in IM2, which shows, in IM2, the C—O bond is formed (see Table 2). The C—Cl stretch mode in TS1 and IM1 are near to each other but this mode in TS2 decreases and reaches to Cl—C—O stretch (453 cm^{-1}) and then disappears at IM2, which shows cleavage of the C—Cl single bond in IM2. The comparison of modes of these species in Table 2 reveals no significant frequency changes for the O—H stretch mode and modes involving CH$_3$ are obtained, so these bonds are not broken upon this path.

Vibrational mode analysis for reaction channels of IM2

The four reaction pathways of IM2 are[1]:

$$IM2 \rightarrow TS6 \rightarrow CH_3O + HCl \qquad (P1)$$

$$\rightarrow TS7 \rightarrow CH_2OH + HCl \qquad (P2)$$

$$\rightarrow TS8 \rightarrow CH_3OCl + H \qquad (P3)$$

$$\rightarrow TS9 \rightarrow ClCH_2OH + H \qquad (P4)$$

The frequencies and vibrational mode assignment of TS6, TS7, TS8, and TS9 are shown in Table 3. The first reaction pathway of IM2 is P1 formation via TS6. The O—H6 stretch mode at 3893 cm^{-1} of IM2 is decreased to i3243 cm^{-1} in TS6, which shows that the O—H6 bond is weakened. In TS6, the only imaginary frequency belongs to this mode (i3243 cm^{-1}), which is relative to the breaking bond. However, the appearance of H6—Cl stretch mode (1092 cm^{-1}) may show the H6—Cl bond is strengthened. The second reaction pathway of IM2 starts with hydrogen atom migration from the methyl group of IM2

Table 1. Vibrational frequencies and vibrational mode assignment for the reactants and products involved in the $CH_3Cl + OH$ reaction.

Species	Frequency	Modes assignment	Species	Frequency	Modes assignment
$CH_3O(C_1)$	806	Whole rock in plane	$CH_2OH(C_1)$	445	Whole rock out of plane
	983	Whole bend in plane		969	CH_2 twist
	1132	C—O stretch		1079	Whole bend in plane
	1424	CH_3 twist		1218	C—O stretch
	1431	CH_3 bend in plane		1380	Whole rock in plane
	1545	H2—C—H4 bend in plane		1518	CH_2 bend in plane
	3016	CH_3 symmetric stretch		3182	CH_2 symmetric stretch
	3099	CH_3 asymmetric stretch		3336	CH_2 asymmetric stretch
	3135	H2—C—H4 asymmetric stretch		3908	O—H7 stretch
$CH_3OCl(C_1)$	267	Whole rock in plane	$ClCH_2OH(C_1)$	358	Whole bend in plane
	370	Whole bend in plane		447	Whole twist
	677	Cl—O stretch		741	C—Cl stretch
	1055	C—O stretch		993	H5—O—CH_2 rock out of plane
	1192	O—CH_3 rock in plane		1125	C—O stretch
	1211	CH_3 rock out of plane		1222	H5—O—CH_2 rock in plane
	1483	CH_3 twist		1393	H5—O—CH_2 twist
	1486	CH_3 bend in plane		1427	H5—O—CH_2 bend in plane
	1524	H2—C—H4 bend in plane		1517	H2—C—H3 bend in plane
	3068	CH_3 symmetric stretch		3124	H2—C—H3 symmetric stretch
	3157	H2—C—H4 asymmetric stretch		3224	H2—C—H3 asymmetric stretch
	3193	C—H3 stretch		3878	O—H7 stretch
$CH_3Cl(C_{3v})$	792	C—Cl stretch	$CH_2Cl(C_{2v})$	140	CH_2 rock out of plane
	1069	CH_3 rock out of plane		943	C—Cl stretch
	1069	CH_3 rock in plane		1056	CH_2 rock in plane
	1445	CH_3 twist		1460	CH_2 bend in plane
	1495	CH_3 bend in plane		3240	CH_2 symmetric stretch
	1495	H3—C—H4 bend in plane		3347	CH_2 asymmetric stretch
	3109	CH_3 symmetric stretch	$OH(C_{\infty v})$	3838	O—H stretch
	3215	H2—C—H3 asymmetric stretch	$H_2O(C_{2v})$	1628	H—O—H bend in plane
	3215	CH_3 asymmetric stretch		3886	H—O—H symmetric stretch
$HCl(C_{\infty v})$	3087	C—O stretch		4005	H—O—H asymmetric stretch
$CH_3(D_{3h})$	461	CH_3 twist	$HOCl(C_s)$	731	O—Cl stretch
	1446	H2—C—H3 bend in plane		1211	H—O—Cl bend in plane
	1446	CH_3 bend in plane		3833	O—H stretch
	3166	CH_3 symmetric stretch			
	3359	H3—C—H4 asymmetric stretch			
	3359	CH_3 asymmetric stretch			

ened. Comparison of modes in Tables 3 and 1 show that the modes in TS9 can exist in products with frequencies similar or near to each other; these comparisons show that the reactions have completely performed.

Vibrational mode analysis for reaction channels of IM1

The three reaction pathways of IM1 are:[1]

$$IM1 \rightarrow TS3 \rightarrow IM3 \rightarrow TS10$$
$$\rightarrow CH_3 + ClOH \quad (P5)$$
$$\rightarrow TS4 \rightarrow CH_2Cl + H_2O \quad (P6)$$
$$\rightarrow TS5 \rightarrow ClCH_2OH + H\cdots \quad (P7)$$

As illustrated in Ref. [1], IM1 can yield product P5 via TS3 and TS10. This pathway consists of two steps. The frequencies and vibrational modes assignment for this channel are shown in Table 4. The Cl atom of CH_3Cl can add to the OH radical via TS3, forming IM3. The imaginary frequency of TS3 belongs to whole bend in plane mode at i329 cm^{-1}. The imaginary frequency and the Cl—O stretch mode (711 cm^{-1}) denote that the O atom has not left the Cl atom completely. For the Cl—O, bond is extended to 2.337 Å, so its stretch mode vanishes. On the other hand, in TS3, the Cl—O bond has been weakened, with rupture of this bond, IM3 will form. The product of this channel is P5 that can form via TS10. In TS10, four whole modes (rock in plane and bend in plane, twist and rock out of plane) and C—Cl—O asymmetric stretch mode at i871 cm^{-1} denote the formation of the Cl—O bond. At the same time, the bond between the C atom and the Cl atom has been weakened. Thus, the imaginary frequency is relative to the forming and broken bonds. In TS10, the disappearance of the C—Cl stretch mode shows that the C—Cl bond has ruptured.

to Cl atom via TS7 to form P2. The imaginary frequency of TS7 at i320 cm^{-1} is assigned to the Cl—H3—C asymmetric stretch mode. The whole bend in plane and its rock in plane mode show the H3 atom is shifting to the terminal Cl atom. Furthermore, almost all CH_3 vibrational modes disappear because the C—H3 bond is elongated to 1.17 Å (see Figure 1) to form P2.
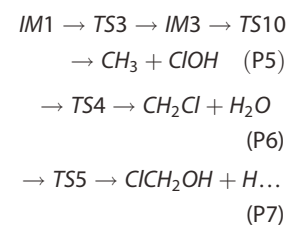
Intermediate IM2 can dissociate to P3 via TS8. In TS8, the only imaginary frequency belongs to the O—H stretch mode (i2277 cm^{-1}), the imaginary frequency is always relative to the bond that is forming or the bond that is rupturing, in this case the imaginary frequency denotes the bond between the O atom and the H atom that has been weakened. As Figure 1 shows, the O—H bond is lengthened by 0.47 Å.

The next reaction channel of IM2 is P4 formation via TS9. For TS9, CH_3 vibrational modes, for example, twist, symmetric stretch, and asymmetric stretch disappear because the C—H4 is elongated and the C—H4 stretch mode frequency becomes imaginary. This mode at 3207 cm^{-1} of IM2 is decreased to i2192 cm^{-1} in TS9, which shows that the C—H4 bond is weak-

In addition, IM1 can produce products P6 and P4. Intermediate IM1 can dissociate to P6 via TS4 that the C—H4—O asymmetric stretch mode has an imaginary frequency. The frequencies and vibrational mode assignment of TS4 are shown in Table 5.

Table 2. Vibrational frequencies and vibrational mode assignment for TS1, IM1, TS2, and IM2.

Species	Frequency	Modes assignment	Species	Frequency	Modes assignment
TS1(C$_1$)	i371	H7—CH$_3$ rock in plane	IM1(C$_1$)	105	Whole rock in plane
	150	Whole twist		109	Whole bend in plane
	174	H7—O twist		307	H7—CH$_3$ rock in plane
	319	Whole bend in plane		484	Whole twist
	480	H7—O rock in plane		582	H7—O rock in plane
	762	C—Cl stretch		760	C—Cl stretch
	1021	CH$_3$ rock out of plane		1056	CH$_3$ rock out of plane
	1047	CH$_3$ rock in plane		1070	CH$_3$ rock in plane
	1418	H2—C—H3 bend in plane		1446	CH$_3$ twist
	1446	CH$_3$ twist		1513	H2—C—H3 bend in plane
	1501	CH$_3$ bend in plane		1521	CH$_3$ bend in plane
	3127	CH$_3$ symmetric stretch		3106	C—H4 stretch
	3217	H2—C—H4 bend in plane		3202	CH$_3$ asymmetric stretch
	3300	C—H3 stretch		3269	H2—C—H3 asymmetric stretch
	3823	O—H7 stretch		3817	O—H7 stretch
TS2(C$_1$)	i1075	C—O stretch	IM2(C$_1$)	80	Whole rock in plane
	109	Whole rock in plane		108	H6—CH$_3$ rock in plane
	276	Whole rock out of plane		195	Whole rock out of plane
	453	Cl—C—O asymmetric stretch		428	H6—O twist
	609	H6—O rock in plane		1063	C—O stretch
	782	H6—O—CH$_3$ rock in plane		1085	H6—O—CH$_3$ bend in plane
	978	Whole rock out of plane		1194	O—CH$_3$ rock in plane
	1058	H6—O—CH$_3$ bend in plane		1369	H6—O—CH$_3$ rock in plane
	1370	CH$_3$ twist		1502	CH$_3$ twist
	1457	H2—C—H3 bend in plane		1518	H3—C—H4 bend in plane
	1519	CH$_3$bend in plane		1528	CH$_3$ bend in plane
	3176	CH$_3$ symmetric stretch		3071	CH$_3$ symmetric stretch
	3320	CH$_3$ asymmetric stretch		3151	H2—C—H3 asymmetric stretch
	3344	H2—C—H3 asymmetric stretch		3207	H4—C stretch
	3823	O—H6 stretch		3893	O—H6 stretch

Table 3. Vibrational frequencies and vibrational mode assignment for TS6, TS7, TS8, and TS9.

Species	Frequency	Modes assignment	Species	Frequency	Modes assignment
TS6(C$_1$)	i3243	O—H6 stretch	TS7(C$_1$)	i320	Cl—H3—C asymmetric stretch
	86	Whole twist		86	Whole bend in plane
	143	Whole rock in plane		204	Whole rock in plane
	188	H6—O—CH$_3$ rock in plane		438	H6—O—CH$_3$ rock in plane
	1054	C—O stretch		1011	H6—O—CH$_3$ twist
	1092	H6—Cl stretch		1092	H6—O—CH$_3$ bend in plane
	1144	H6—CH$_3$ bend in plane		1143	H3—CH$_2$ rock in plane
	1195	H6—CH$_3$ rock out of plane		1277	H6—O—C—H2 bend in plane
	1428	H6—CH$_3$ twist		1334	H6—C—H3 rock in plane
	1481	CH$_3$ twist		1405	H6—C—H3 bend in plane
	1493	CH$_3$ bend in plane		1502	H2—C—H4 bend in plane
	1529	H3—C—H4 bend in plane		1709	C—H3 stretch
	3051	CH$_3$ symmetric stretch		3100	H2—C—H4symmetric stretch
	3136	H3—C—H4 asymmetric stretch		3213	H2—C—H4asymmetric stretch
	3146	CH$_3$ asymmetric stretch		3888	O—H6 stretch
TS8(C$_1$)	i2277	O—H7 stretch	TS9(C$_1$)	i2191	H4—C stretch
	185	H7—O—CH$_3$ rock in plane		121	Whole rock in plane
	254	Whole rock out of plane		297	H4—C—Cl stretch
	347	Whole twist		482	H6—O-C bend in plane
	572	H7—C bend in plane		674	H6—O—C rock out of plane
	892	Whole bend in plane		819	H4—CH$_2$ bend in plane
	1081	C—O stretch		999	H6—C—H4 rock in plane
	1181	H3—C—H4 rock in plane		1130	H6—CH$_2$bend in plane
	1198	CH$_3$ rock in plane		1266	C—O stretch
	1467	CH$_3$ twist		1315	H4—CH$_2$bend in plane
	1495	H2—C—H4 bend in plane		1404	H6—CH$_2$rock in plane
	1516	H3—C—H4 bend in plane		1547	H2—C—H3 bend in plane
	3098	CH$_3$ symmetric stretch		3154	H2—C—H3 symmetric stretch
	3200	H3—C—H4 asymmetric stretch		3228	H2—C—H3 asymmetric stretch
	3325	C—H2 stretch		3861	O—H6 stretch

The final pathway from IM1 is forming product P4 via TS5. The assignment of frequencies and vibrational modes for TS5 is shown in Table 4. For TS5, the imaginary frequency belongs to the C—H4 stretch mode. When the H4 atom leaves from CH$_3$Cl to produce P4, all vibrational modes involved C—H4 bond of TS5 vanish (e.g., CH$_3$ rock in plane, CH$_3$ twist, CH$_3$ rock out of plane, and CH$_3$ bend in plane), which shows this bond is completely broken.

It is worth noting that all species involved in reaction have CH$_3$ twist mode with frequencies near to each other, whereas, because of H abstraction from CH$_3$ group in reaction path, one can not see this mode in species TS9, TS7, TS5, and TS4.

Because the dominant channel is the production of P6,[1] we present the variations of generalized mode vibrational frequencies along the minimum energy path (MEP) for this channel in Figure 2. In the negative limit of s ($s = -\infty$), the frequencies correspond to the reactants, while in the positive limit of s ($s = +\infty$), the frequencies are associated with the products. The C—H4—O asymmetric stretch mode shown by the solid line 3 in this figure relates to the breaking of C—H4 bond in IM1 region (the C—H4 stretch mode at 3106 cm^{-1}), and the formation of H4—O bond in the products region (H$_2$O) changes sharply in the region from $s = -1.0$ to 1.0 (amu)$^{1/2}$ bohr.

Table 4. Vibrational frequencies and vibrational mode assignment for TS3, IM3, TS10, and TS5.

Species	Frequency	Modes assignment	Species	Frequency	Modes assignment
TS3(C_1)	i329	Whole bend in plane	IM3(C_1)	45	Whole rock in plane
	47	Whole rock in plane		90	Whole bend in plane
	347	H7—CH$_3$ bend in plane		155	Whole twist
	503	Whole twist		283	C—Cl—O asymmetric stretch
	711	Cl—O stretch		513	H7—CH$_3$ bend in plane
	820	H7—CH$_3$ rock in plane		606	C—Cl stretch
	859	H7—CH$_3$ bend in plane		1012	CH$_3$ rock out of plane
	895	CH$_3$ rock in plane		1016	CH$_3$ rock in plane
	1257	CH$_3$ twist		1382	CH$_3$ twist
	1448	H2—C—H6 bend in plane		1480	H3—C—H4 bend in plane
	1455	H2—C—H3 bend in plane		1484	H2—C—H3 bend in plane
	3146	CH$_3$ symmetric stretch		3127	CH$_3$ symmetric stretch
	3321	CH$_3$ asymmetric stretch		3252	C—H4 stretch
	3330	H2—C—H6 asymmetric stretch		3254	H2—C—H3 asymmetric stretch
	3768	O—H7 stretch		3849	O—H7 stretch
TS10(C_1)	i871	C—Cl—O asymmetric stretch	TS5(C_1)	i1671	C—H4 stretch
	96	Whole rock in plane		258	H7—O—C twist
	169	Whole bend in plane		320	Whole twist
	185	Whole twist		576	Whole rock in plane
	209	Whole rock out of plane		733	C—Cl stretch
	506	CH$_3$ rock out of plane		770	Whole bend in plane
	561	H2—C—H3 rock out of plane		956	H7—CH$_2$ rock out plane
	954	CH$_3$ twist		1010	H4—CH$_2$ rock in plane
	1098	H7—O rock in plane		1050	H7—O—C rock in plane
	1443	H2—C—H4 bend in plane		1326	H7—CH$_2$ twist
	1449	H2—C—H3 bend in plane		1424	H7—CH$_2$ bend in plane
	3162	CH$_3$ symmetric stretch		1618	H7—CH$_2$ rock in plane
	3346	CH$_3$ asymmetric stretch		2978	H2—C—H3 symmetric stretch
	3355	H2—C—H3 asymmetric stretch		3163	H2—C—H3 asymmetric stretch
	3858	C—H7 stretch		3824	O—H7 stretch

Table 5. Vibrational frequencies and vibrational mode assignment for TS4.

Mode number	Frequency	Modes assignment
3	i1944(C_1)	C—H4—O asymmetric stretch
13	60	H7—O bend in plane
14	115	Whole rock in plane
15	265	Whole twist
12	732	Whole bend in plane
10	790	H4—C—Cl asymmetric stretch
11	856	C—Cl stretch
9	1044	H4—CH$_2$ rock in plane
8	1134	H7—H4—CH$_2$ twist
7	1274	H3—C—H4 bend in plane
6	1451	H7—H4—CH$_2$ rock out of plane
5	1470	H2—C—H3 bend in plane
4	3154	H2—C—H3 symmetric stretch
2	3252	H2—C—H3 asymmetric stretch
1	3829	O—H7 stretch

after the saddle point, it changes maximum in the region from $s = -0.5$ to 1.0 (amu)$^{1/2}$ bohr, which shows the whole bend in plane mode. The two lowest frequencies (14 and 15 lines) are maximum near the saddle point and tend to be zero for reactants and products. These changes should cause large decreases in the zero point energy (ZPE; Figure 4 in Ref. [1]). These comparisons show that this reaction has been performed completely. The other frequencies do not change significantly in going from the reactants to products.

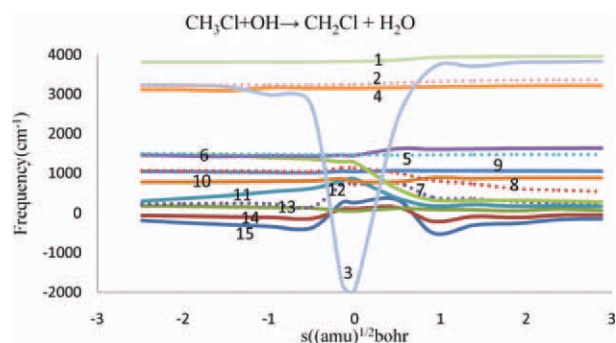Furthermore, to decide whether TS4 has a product- or reactant-like character, the following parameter L was used:[5]

$$L = \frac{l_{C_1-H_4}(TS4) - l_{C_1-H_4}(CH_3Cl)}{l_{H_4-O_6}(TS_4) - l_{H_4-O_6}(H_2O)} \quad (1)$$

here $l_{i-j(k)}$ denotes the length of the i–j bond in the species k (reactant, product, TS). An L value less than unity predicts a reactant-like charac-

Figure 2. Change of the generalized mode vibrational frequencies for the $CH_3Cl + OH \rightarrow CH_2Cl + H_2O$ reaction as functions of the reaction coordinates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In the saddle point ($s = 0$), TS4, three whole modes (rock in plane and bend in plane and twist) and two modes of asymmetric stretch (C—H4—O at i1944 cm^{-1} and H4—C—Cl at 790 cm^{-1}) denote the formation of the H4—O bond. Thus, the imaginary frequency is relative to the forming bond H4—O and the breaking bond C—H4. The line 7 indicates the CH$_3$ twist mode (at 1446 cm^{-1}) in IM1 and it drops linearly after the saddle point and goes to zero for products, this decrease shows H4 has been added to the oxygen atom. The line 11 represents the C—Cl stretch mode which its frequency increases in IM1 region, and after the saddle point becomes linearly. The line 12 drops

ter, whereas an L value greater than 1 denotes a product-like TS. In this particular case, L is 0.27; it means TS4 has a reactant-like character. Comparison of modes of species associated with the main pathway (reactants, IM1, TS4, and P6) relies that TS has a reactant-like character; it means this reaction is exothermic.

Conclusion

The reaction mechanism of CH$_3$Cl with Cl has been investigated thoroughly via the vibrational model analysis. The relationships among the reactants, 10 TSs, three intermediates,

and various products involving this multichannel reaction are elucidated. The vibrational mode analysis shows that the reaction mechanism is reliable.

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