We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

4,300
Open access books available

116,000
International authors and editors

130M
Downloads

154
Countries delivered to

TOP 1%
Our authors are among the most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Abstract

In this chapter, we presented a short review of past and present experimental and theoretical work on the reactions of the transition metal monoxide and dioxide molecules with monochloromethane in excess argon matrices. A series of infrared absorption spectra combining with density functional theoretical (DFT) calculation characterized that the transition metal monoxide molecules produced by laser-ablated higher oxides activated C–H and C–Cl bonds of CH$_3$Cl to first form the weakly bound MO(CH$_3$Cl) (M = Sc, Y, Nb, Ta, Ti, Zr, Mn, Fe) complexes, which further photoisomerized to the more stable chlorine-transfer (Cl-transfer) CH$_3$OMCl (M = Sc, Y), CH$_3$M(O)Cl (M = Ti, Zr), CH$_3$MOCl (M = Mn, Fe), and agostic hydrogen-transfer (H-transfer) CH$_2$ClMOH (M = Sc, Y, Nb, Ta) products upon limited light excitation. Transition metal dioxides reaction with CH$_3$Cl also formed MO$_2$(CH$_3$Cl) (M = Ti, Zr, Nb, Ta) complexes, which were further rearranged to the more stable Cl-transfer CH$_3$OM(O)Cl (M = Ti, Zr) and agostic H-transfer CH$_2$ClM(O)OH (M = Nb, Ta) molecules between the metal center atom and the chlorine atom upon ultraviolet light irradiation. Their different reactivity was interpreted according to the different valence electrons of metal center.

Keywords: monochloromethane, chlorine transfer, hydrogen transfer, transition metal oxides, agostic interaction

1. Introduction

Monochloromethane, as the one of the simplest halohydrocarbons, also called methyl chloride, plays an important role in the industrial, synthetic, materials chemistry. It is always regarded
that monochloromethane is the largest natural source of ozone-depleting chlorine compounds and accounts for about 15% of the present atmospheric chlorine content as one kind of chlorinated volatile organic compounds (CVOCs). At present, monochloromethane is observed in the dry leaf with the content of 0.1–0.3 μg/g/h, and large emissions of monochloromethane are observed from some common certain types of ferns and dipterocarpaceae [1, 2]. Monochloromethane is also industrially produced by the oxidation and chlorination reaction of methane in the presence of metal chloride catalyst, and drying monochloromethane conversed to gasoline and olefins on the methanol to gasoline (MTG) and the methanol to olefins (MTO) catalysts [3, 4]. The conversion of methyl chloride to hydrocarbons has been investigated since the mid-1980s [5]. The product distribution of methyl chloride to hydrocarbons is strikingly similar to methanol conversion over the same topology [6]. Recently several ZSM-5 zeolites and SAPO sieves catalysts were reported the high performances on the catalytic conversion of monochloromethane to light olefins [7–9]. Modified SAPO-34 catalysts were also chosen to enhance its catalytic performance for the conversion of chloromethane to light olefins [10–13]. The oxidation addition of metal into carbon-halogen bonds is a key step in many stoichiometric and catalytic reactions. Activation of compounds containing C─X (X = Cl, Br, I) bonds attracts widespread interest due to the underactive organic functional group and the inherent chemical properties. Predominantly alkyl and aryl halides are extensively applied as electrophiles in the transition metal-catalyzed cross-coupling reactions [14–16]. It has a far-reaching significance on carbon-chlorine (C─Cl) bond catalytic oxidation on the conversion of monochloromethane to gasoline and olefins.

Scheme 1. The reactivity of transition metal monoxide and dioxide with monochloromethane in argon from Refs. [27–30].

The reactions of transition metal centers with chloromethane may serve as the simplest model for understanding the intrinsic mechanism of the organic halides catalytic oxidation processes. The reactions on transition metal atoms with monochloromethane have been intensively studied in solid noble gas matrices. Investigations have reported that C─X bond of CH₂X (X = F, Cl, Br, I) are activated by transition metal atoms [17–22]. The higher valence of group 6 metals can form the methylidyne complexes CH = MH₂X (M = Mo, W, X = H, F, Cl, Br) [23–26]. In this chapter, the reactions of simple transition-metal oxide molecules with monochloromethane in
solid argon were reviewed using matrix infrared absorption spectroscopy and density functional theoretical (DFT) calculations. As shown in Scheme 1, the ground-state transition metal monoxide molecules activated carbon-hydrogen (C─H) and C─Cl bond of CH₃Cl upon a certain wavelength excitation in argon matrices. The weakly bound MO(CH₃Cl) (x = 1, 2; M = Sc, Y, Nb, Ta, Ti, Zr, Mn, Fe) complexes were initially formed and then isomerized to the more stable Cl-transfer CH₃OMCl (M = Sc, Y) and CH₃M(O)Cl (M = Ti, Zr, Nb, Ta, Mn, Fe), and agostic H-transfer CH₂ClMOH (M = Sc, Y, Nb, Ta) isomers upon limited visible light excitation. The MO₂(CH₃Cl) (M = Ti, Zr, Nb, Ta), which were formed from the reactions on MO₂ with CH₃Cl, were further rearranged to the more stable Cl-transfer CH₃OM(O)Cl (M = Ti, Zr) and H-transfer CH₂ClM(O)OH (M = Nb, Ta) molecules with agostic interactions between the chlorine and the metal center under ultraviolet light irradiation.

2. Experimental and computational methods

The experimental setup for pulsed laser-ablated and matrix isolation Fourier transform infrared (FTIR) spectroscopic technique has been previously described in detail [31]. Briefly, the 1064 nm Nd:YAG laser fundamental (Spectra Physics, DCR 150, 20 Hz repetition rate, and 8 ns pulse width) was focused onto the rotating bulk metal oxide targets, which were prepared by sintered metal oxide powders. Laser-evaporation of bulk higher metal oxide targets has been proved to be an extensively available technique to prepare pure metal oxides in noble gas matrices [32–34]. Using standard manometric technique, the CH₃Cl/Ar samples were mixed at a proper proportion in a stainless steel vacuum line. The CH₃Cl sample was subjected to several freeze-pump-thaw cycles at 77 K before use. The laser-evaporated species were co-deposited with chloromethane in excess argon onto a CsI window cooled normally to 6 K by a closed-cycle helium refrigerator (ARS, 202N). The matrix samples were deposited at a rate of approximately 5 mmol/h for 1–2 h. Isotopic-labeled ¹³CH₃Cl and CD₃Cl (ISOTEC, 99%) were used without further purification. Infrared spectra between 450 and 4000 cm⁻¹ were recorded on a Bruker IFS 66v/s spectrometer using HgCdTe (MCT) detector cooled by liquid N₂ at 0.5 cm⁻¹ resolution. Samples were annealed to different temperatures and cooled back to 6 K to acquire the spectra, and selected samples were subjected to visible or broadband irradiation using a 250 W high-pressure mercury arc lamp with selected wavelength glass filters.

Density functional theoretical calculations were performed by using Gaussian 03 programs [35] to identify the experimental assignments. The three-parameter hybrid functional, according to Becke with additional correlation corrections from Lee, Yang, and Parr (B3LYP), was utilized [36, 37] to optimize ground geometries, calculate frequencies, and derive the zero-point vibrational energies. Transition-state optimizations were performed with the Berny geometry optimization algorithm at the B3LYP level. The 6-311++G(d, p) basis set was used for the H, C, O, Cl, Sc, Ti, Mn, and Fe atoms [38, 39], DGDZVP basis set for Y, Zr, and Nb atoms [40, 41], and the scalar-relativistic SDD pseudopotential and basis set for Ta atom [42, 43]. In addition, the CCSD(T) method was also applied to accurately calculate the single-point energies of the B3LYP-optimized structures with the same basis sets [44].
3. Transition metal monoxides reaction with CH$_3$Cl

Reaction of transition metal monoxides (ScO, YO, TiO, ZrO, NbO, TaO, MnO, FeO) with monochloromethane was investigated in solid argon by infrared absorption spectroscopy, combining with isotopic substituted experiments and theoretical calculations. The initial reaction step is the formation of the MO(CH$_3$Cl) (M = Sc, Y, Ti, Zr, Nb, Ta, Mn, Fe) complex with metal atom bound with chlorine atom and/or oxygen atom with H atoms on annealing. Upon a certain wavelength photolysis, the MO(CH$_3$Cl) complex was isomerized by the insertion of the $\text{M=N=O}$ to $\text{C─H}$ and/or $\text{C─Cl/Cl─C}$ bond. Selected region of infrared spectra is illustrated in Figures 1–4.

Figure 1. Difference spectra in the selected regions scandium monoxide with isotopic substituted chloromethane in excess argon. (Spectrum taken after 15 min of broadband irradiation minus spectrum taken after 25 K annealing). (a) 0.5% CH$_3$Cl, (b) 0.5% $^{13}$CH$_3$Cl, and (c) 0.5% CD$_3$Cl. (Reprinted with the permission from Ref. [27]. Copyright 2013 American Chemical Society).

Figure 2. Difference spectra in the selected regions from co-deposition of a laser-ablated TiO$_2$ target in excess argon. Spectrum taken after 15 min of full-arc broadband photolysis irradiation ($\lambda < 300$ nm) followed by the 25 K annealing minus spectrum taken after sample annealing at 25 K. (a) 0.5% CH$_3$Cl, (b) 0.5% $^{13}$CH$_3$Cl, and (c) 0.5% CD$_3$Cl. (Reprinted with the permission from Ref. [28]. Copyright 2013 American Chemical Society).
In both the scandium and yttrium experiments, two MO(CH₃Cl) (M = Sc, Y) complex isomers were formed spontaneously on annealing [27]. These absorptions of MO(CH₃Cl) (M = Sc, Y) complex are observed at 898.4 and 919.1 cm⁻¹ for Sc, and 1050.9, 805.9, and 784.8 cm⁻¹ for Y, as shown in Table 1, which are corresponding to the Sc─O and Y─O vibration frequencies. The CH₃OMCl and CH₃C1MOH (M = Sc, Y) molecules were produced from the weakly bound MO(CH₃Cl) complexes through photoinduced isomerization reactions on 250–300 nm wavelength irradiation, as shown in Figure 1. The CH₂OMCl (M = Sc, Y) isomer observed at
1171.5 and 565.6 cm\(^{-1}\) for Sc and 1149.2 and 490.9 cm\(^{-1}\) for Y can be regarded as being formed through the addition of the C─Cl bond to the O═M bond, whereas the CH\(_3\)CIMOH (M = Sc, Y) isomer observed at 3775.0 and 738.4 for Sc, and 3774.2 and 627.6 for Y is formed through the addition of the C─H bond to the M═O bond. On the basis of DFT calculations, the MO(CH\(_3\)Cl) (M = Sc, Y) complex with C\(_s\) structure is more stable than the complex with C\(_{3v}\) structure by 25.5 (Sc) or 24.0 (Y) kJ/mol. Both CH\(_3\)OMCl and CH\(_3\)CIMOH (M = Sc, Y) molecules are more stable than the MO(CH\(_3\)Cl) complex isomers. The CH\(_3\)OMCl (M = Sc, Y) molecule was predicted to proceed through a transition state with an energy barrier of 17.7 for Sc and 8.4 kJ/mol for Y from the MO(CH\(_3\)Cl) complex, whereas the CH\(_2\)ClMOH isomer also proceeded through a transition state with a much higher energy barrier of 160.1 for Sc and 178.5 kJ/mol for Y from the MO(CH\(_3\)Cl) complex. The CH\(_3\)OMCl (M = Sc, Y) structure is about 173.0 for Sc and 180.6 kJ/mol for Y lower in energy than the CH\(_2\)ClScOH and CH\(_2\)ClYOH isomer. The CH\(_2\)ClMOH (M = Sc, Y) molecule was also calculated to involve agostic interaction observed between the metal atom and the chlorine atom due to short bond distances of 2.598 Å for Sc─Cl and 2.821 Å for Y─Cl. Such interaction is quite similar to the agostic interactions generally defined to characterize the distortion of an organometallic moiety, which brings an appended C─H bond into close proximity with the metal center [17, 21, 45].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ground state</th>
<th>Point group</th>
<th>Vibrational frequency(^a)</th>
<th>Binding energy(^c)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScO(CH(_3)Cl)</td>
<td>2(^{A'})</td>
<td>C(_s)</td>
<td>898.4</td>
<td>−34.9</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>2(^{A_1})</td>
<td>C(_{3v})</td>
<td>919.1</td>
<td>−9.4</td>
<td></td>
</tr>
<tr>
<td>YO(CH(_3)Cl)</td>
<td>2(^{A'})</td>
<td>C(_s)</td>
<td>1050.9, 783.5</td>
<td>−37.0</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>2(^{A_1})</td>
<td>C(_{3v})</td>
<td>805.9</td>
<td>−13.0</td>
<td></td>
</tr>
<tr>
<td>TiO(CH(_3)Cl)</td>
<td>3(^{A'})</td>
<td>C(_s)</td>
<td>961.8</td>
<td>−41.4</td>
<td>[28]</td>
</tr>
<tr>
<td>ZrO(CH(_3)Cl)</td>
<td>3(^{A})</td>
<td>C(_1)</td>
<td>898.2</td>
<td>−40.5</td>
<td>[28]</td>
</tr>
<tr>
<td>NbO(CH(_3)Cl)</td>
<td>4(^{A'})</td>
<td>C(_s)</td>
<td>933.6</td>
<td>−29.5</td>
<td>[29]</td>
</tr>
<tr>
<td>TaO(CH(_3)Cl)</td>
<td>2(^{A})</td>
<td>C(_1)</td>
<td>991.5</td>
<td>−5.0</td>
<td>[29]</td>
</tr>
<tr>
<td>MnO(CH(_3)Cl)</td>
<td>4(^{A'})</td>
<td>C(_s)</td>
<td>843.4</td>
<td>−38.9</td>
<td>[30]</td>
</tr>
<tr>
<td>FeO(CH(_3)Cl)</td>
<td>3(^{A'})</td>
<td>C(_s)</td>
<td>882.7</td>
<td>−97.4</td>
<td>[30]</td>
</tr>
</tbody>
</table>

\(^a\) Only the values for the most abundant metal isotope are listed.
\(^b\) The mode assignments of the experimental vibrational frequencies are discussed in the cited literature.
\(^c\) Relative to the energy sum of ground metal oxide and CH\(_3\)Cl.

Table 1. Ground electronic states, symmetry point groups, vibrational frequencies (cm\(^{-1}\)) and binding energies (kJ/mol) for the MO(CH\(_3\)Cl) species in solid argon.

For IVB metal monoxides, the ground-state MO(CH\(_3\)Cl) (M = Ti, Zr) complexes correlate to the ground-state TiO (\(^3\)\(\Delta\)) and ZrO (\(^1\)\(\Sigma\)\(^−\)). The binding energies are predicted to be 20.5 (Ti) and 12.2 kcal/mol (Zr), which are larger than the corresponding values of TiO(CH\(_4\)) and ZrO(CH\(_4\)) [45, 46]. The MO(CH\(_3\)Cl) (M = Ti, Zr) complexes can rearrange to the CH\(_3\)M(O)Cl isomers by metal terminal insertion to C─Cl bond upon UV light irradiation (\(\lambda < 300\) nm), which are
observed at 999.5 and 526.2 cm$^{-1}$ for Ti, and 915.2 and 488.3 cm$^{-1}$ for Zr, as shown in Figure 2. Theoretical calculations also indicated that the electronic state crossings exist from the MO (M = Ti, Zr) + CH$_3$Cl reaction to the more stable CH$_3$M(O)Cl molecules through the MO(CH$_3$Cl) complexes traverse their corresponding transition states. The CH$_3$M(O)Cl (M = Ti, Zr) molecule was predicted to have a singlet ground state without symmetry. According to CCSD(T) single-point calculations on B3LYP optimization geometry, the singlet ground state is 44.3 kcal/mol for CH$_3$Ti(O)Cl and 52.2 kcal/mol for CH$_3$Zr(O)Cl lower in energy than its corresponding triplet state. The triplet MO(CH$_3$Cl) (M = Ti, Zr) isomerized to the singlet CH$_3$M(O)Cl (M = Ti, Zr) molecule through their corresponding transition states, which indicated that these reactions related to the spin crossing under UV light irradiation.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ground state</th>
<th>Point group</th>
<th>Vibrational frequency$^b$</th>
<th>Binding energy$^c$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OsCl</td>
<td>$^3A$</td>
<td>$C_1$</td>
<td>1171.5, 565.6</td>
<td>−268.8</td>
<td>[27]</td>
</tr>
<tr>
<td>CH$_3$ClScOH</td>
<td>$^3A$</td>
<td>$C_1$</td>
<td>3775.0, 738.4</td>
<td>−95.8</td>
<td>[27]</td>
</tr>
<tr>
<td>CH$_3$OYCl</td>
<td>$^3A$</td>
<td>$C_1$</td>
<td>1149.2, 490.9</td>
<td>−300.3</td>
<td>[27]</td>
</tr>
<tr>
<td>CH$_3$CYOH</td>
<td>$^3A$</td>
<td>$C_1$</td>
<td>3774.2, 627.6</td>
<td>−119.7</td>
<td>[27]</td>
</tr>
<tr>
<td>CH$_3$Ti(O)Cl</td>
<td>$^3A$</td>
<td>$C_1$</td>
<td>999.5, 526.2</td>
<td>−324.1</td>
<td>[28]</td>
</tr>
<tr>
<td>CH$_3$Zr(O)Cl</td>
<td>$^3A$</td>
<td>$C_1$</td>
<td>915.2, 488.3</td>
<td>−349.0</td>
<td>[28]</td>
</tr>
<tr>
<td>CH$_3$CINb(O)H</td>
<td>$^3A$</td>
<td>$C_1$</td>
<td>1698.0, 985.0</td>
<td>−136.7</td>
<td>[29]</td>
</tr>
<tr>
<td>CH$_3$CTa(O)H</td>
<td>$^3A$</td>
<td>$C_1$</td>
<td>1760.0, 984.8</td>
<td>−182.7</td>
<td>[29]</td>
</tr>
<tr>
<td>CH$_3$MnOCl</td>
<td>$^3A$</td>
<td>$C_1$</td>
<td>569.6, 542.2</td>
<td>−55.2</td>
<td>[30]</td>
</tr>
<tr>
<td>CH$_3$FeOCl</td>
<td>$^3A$</td>
<td>$C_1$</td>
<td>570.4, 561.5</td>
<td>−50.2</td>
<td>[30]</td>
</tr>
</tbody>
</table>

$^a$ Only the values for the most abundant metal isotope are listed.

$^b$ The mode assignments of the experimental vibrational frequencies are discussed in the cited literature.

$^c$ Relative to the energy sum of ground metal oxide and CH$_3$Cl.

Table 2. Ground electronic states, symmetry point groups, vibrational frequencies (cm$^{-1}$), and binding energies (kJ/mol) for the isomers of MO(CH$_3$Cl) in solid argon.

The ground-state NbO(CH$_3$Cl) and TaO(CH$_3$Cl) molecules are related to the ground-state NbO ($^2\Sigma$) and TaO ($^2\Delta$). The predicted binding energies of 29.5 (Nb) and 5.0 kJ/mol (Ta) are larger than the corresponding values of NbO(CH$_4$) and TaO(CH$_4$) complexes [46], which were predicted to be very weakly interaction with the metal atom being bound to three hydrogen atoms of CH$_4$. The MO(CH$_3$Cl) (M = Nb, Ta) complexes rearranged to the more stable doublet CH$_2$CIM(O)H isomer upon visible light excitation, as shown in Table 2. Thus, some excited states may be involved during the reaction process. The CH$_2$CIM(O)H molecules were predicted to involve agostic interactions between the chlorine atom and the metal center. It is quite interesting to note that the CH$_2$CIM(O)H (M = Nb, Ta) molecules involve agostic interactions between the chlorine atom and the metal atom. It is notable that the group 5 metal methylidene complexes are more agostically distorted than the group 4 metal complexes.
Taking CH\textsubscript{2}ClNb(O)H as an example, the \(\angle\)ClCNb was predicted to be only 80.4° with a Cl--Nb distance of 2.624 Å. Agostic distortion interaction is a universal phenomenon in the structures of the early transition metal alkylidene complexes and even more popular in the structures of the small methylidene complexes, in which agostic interactions are also observed between the group 4–6 transition metal atom and one of the R-hydrogen atoms.

The reactions of FeO and MnO with CH\textsubscript{3}Cl first formed the MO(CH\textsubscript{3}Cl) (M = Mn, Fe) complexes when annealing, which can isomerize to CH\textsubscript{3}MOCl (M = Mn, Fe) upon 300 < \(\lambda\) < 580 nm irradiation. The products were characterized by isotopic IR studies with CD\textsubscript{3}Cl and \(^{13}\)CH\textsubscript{3}Cl and density functional calculations, as shown in Figure 3. Based on theoretical calculations, the MO(CH\textsubscript{3}Cl) (M = Mn, Fe) complexes have \(^4\)A' for Fe and \(^6\)A' ground state for Mn with C\textsubscript{s} symmetry, respectively, as listed in Table 1. The binding energies of MO(CH\textsubscript{3}Cl) (M = Mn, Fe) are 9.3 and 23.3 kcal/mol lower than MO + CH\textsubscript{3}Cl, which are higher in energy than MO(CH\textsubscript{4}) and MO(Ng) (Ng = Ar, Kr, Xe) at the same calculation level [46–48]. The accurate CCSD(T) single-point calculations illustrate the CH\textsubscript{3}MOCl isomerism are 13.8 and 3.1 kcal/mol lower in energy than the MO(CH\textsubscript{3}Cl) (M = Mn, Fe) complexes.

The different reactivity of metal monoxide with CH\textsubscript{3}Cl can be rationalized in terms of changes in valence electron structures accompanied by electronic spin state crossing. In the scandium and yttrium reactions, the ground ScO and YO molecules reacted with CH\textsubscript{3}Cl to form two isomeric MO(CH\textsubscript{3}Cl) (M = Sc, Y) complexes spontaneously on annealing. Broad-band irradiation produced either the addition of the C--Cl bond to the O=<M (M = Sc, Y) bond to form the CH\textsubscript{3}OMCl (M = Sc, Y) molecules with +II oxidation state of center metal or the addition of the C--H bond to the M=O bond to give the CH\textsubscript{2}ClMOH isomer with the valence of metal remaining in +II oxidation state. The CH\textsubscript{2}ClMOH (M = Sc, Y) include one \(\alpha\)-chlorine atom to form agostic molecules between chlorine atom and metal center atom with less than 90° of \(\angle\)ClCM and short Cl---M (M = Sc, Y) distances. No \(\alpha\)-H and/or \(\alpha\)-Cl atom for the MO(CH\textsubscript{3}Cl) complex exist, so no agostic interaction is observed. Sc and Y have only three valence electrons, and hence they are not able to form high oxidation state structures. However, Mn and Fe have five and six valence electrons. Because their d orbitals are fully half-filled and hence are not easily lost, upon 300 < \(\lambda\) < 580 nm irradiation the MO(CH\textsubscript{3}Cl) (M = Mn, Fe) complexes triggered the addition of the C--Cl bond to the M=O bond to form the CH\textsubscript{3}ClMOH isomers with the oxidation states of the metal increasing from the +II to +IV. However, the Nb and Ta have five valence electrons, and they cannot form +V oxidation structures, but possessing one valence electron characteristic of the agnostic chlorine effect.

4. Transition metal dioxides reaction with CH\textsubscript{3}Cl

The ground-state MO\textsubscript{2} (M = Ti, Zr, Nb, Ta) molecules react with CH\textsubscript{3}Cl to first form the weakly bound MO\textsubscript{2}(CH\textsubscript{3}Cl) complexes with O--H and M--Cl bonds. For Ti and Zr, the MO\textsubscript{2}(CH\textsubscript{3}Cl)
complexes can isomerize to the more stable CH$_3$OM(O)Cl molecules with the addition of the C─Cl bond of CH$_3$Cl to one of the O═M bond of MO$_2$ on annealing after broadband light irradiation ($\lambda < 300$ nm), as shown in Figures 2 and 4. And the reaction potential energy profile interpreted the chemical reaction mechanism of C─Cl activation by MO$_2$ (M = Ti, Zr). The photoisomerization reaction of MO$_2$(CH$_3$Cl) (M = Nb, Ta) is quite different from those of MO$_2$(CH$_3$Cl) (M = Ti, Zr). The MO$_2$(CH$_3$Cl) (M = Nb, Ta) complexes were initiated H-transfer under ultraviolet light irradiation to isomerize the more stable CH$_2$ClM(O)OH molecules. The CH$_2$ClM(O)OH (M = Nb, Ta) molecules were predicted to involve agostic interactions between the chlorine atom and the metal center. During the photoisomerization process, no electronic spin state crossings were found, as shown in Table 3, different from the reaction of metal monoxides with CH$_3$Cl.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ground state</th>
<th>Point group</th>
<th>Vibrational frequency$^b$</th>
<th>Binding energy$^c$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$(CH$_3$Cl)</td>
<td>$^1$A</td>
<td>C$_v$</td>
<td>940.3, 906.2</td>
<td>-95.7</td>
<td>[28]</td>
</tr>
<tr>
<td>ZrO$_2$(CH$_3$Cl)</td>
<td>$^1$A$'$</td>
<td>C$_s$</td>
<td>874.1, 804.2</td>
<td>-84.4</td>
<td>[28]</td>
</tr>
<tr>
<td>NbO$_2$(CH$_3$Cl)</td>
<td>$^2$A</td>
<td>C$_v$</td>
<td>948.1, 890.9</td>
<td>-75.66</td>
<td>[29]</td>
</tr>
<tr>
<td>TaO$_2$(CH$_3$Cl)</td>
<td>$^2$A$'$</td>
<td>C$_s$</td>
<td>948.4, 890.8</td>
<td>-52.9</td>
<td>[29]</td>
</tr>
<tr>
<td>CH$_3$OTi(O)Cl</td>
<td>$^1$A</td>
<td>C$_v$</td>
<td>1173.0, 1102.6, 634.1</td>
<td>-326.0</td>
<td>[28]</td>
</tr>
<tr>
<td>CH$_3$OZr(O)Cl</td>
<td>$^1$A</td>
<td>C$_v$</td>
<td>1153.1, 901.2</td>
<td>-331.9</td>
<td>[28]</td>
</tr>
<tr>
<td>CH$_2$ClNb(O)OH</td>
<td>$^2$A</td>
<td>C$_v$</td>
<td>3678.4, 979.4, 712.8</td>
<td>-185.5</td>
<td>[29]</td>
</tr>
<tr>
<td>CH$_2$Clta(O)OH</td>
<td>$^2$A</td>
<td>C$_v$</td>
<td>3690.8, 975.9, 605.8, 495.7</td>
<td>-171.8</td>
<td>[29]</td>
</tr>
</tbody>
</table>

$^a$ Only the values for the most abundant metal isotope are listed.

$^b$ The mode assignments of the experimental vibrational frequencies are discussed in the cited literature.

$^c$ Relative to the energy sum of ground metal oxide and CH$_3$Cl.

Table 3. Ground electronic states, symmetry point groups, vibrational frequencies (cm$^{-1}$), and binding energies (kJ/mol) for the product from MO$_2$ + CH$_3$Cl in solid argon.$^a$.

5. Conclusion and outlook

C─Cl and/or C─H bond of monochloromethane activation by transition metal monoxide and dioxide molecules has been investigated using matrix infrared spectroscopy in excess argon and density functional theoretical calculations. The metal monoxide and dioxide molecules prepared by laser-ablated bulk higher oxide targets reacted with monochloromethane to form the weakly bound MO(CH$_3$Cl) ($x = 1, 2$; M = Sc, Y, Nb, Ta, Ti, Zr, Mn, Fe) complexes, which
isomerized to the more stable CH$_3$OMCl (M = Sc, Y), agostic CH$_2$CIMOH (M = Sc, Y, Nb, Ta) and CH$_3$M(O)Cl (M = Ti, Zr, Nb, Ta, Mn, Fe) isomers upon limited visible light excitation. Metal dioxides also reacted with CH$_3$Cl to form MO$_2$(CH$_3$Cl) (M = Ti, Zr, Nb, Ta), which was rearranged to the more stable CH$_3$OM(O)Cl (M = Ti, Zr) and CH$_2$CIM(O)OH (M = Nb, Ta) molecules under ultraviolet light irradiation. Agostic interactions were observed in CH$_3$CIMOH (M = Sc, Y, Nb, Ta) and CH$_2$ClM(O)OH (M = Nb, Ta) between the chlorine atom and the metal center atom.

Acknowledgements

We gratefully acknowledge the financial support from National Natural Science Foundation of China (Grants No. 21273202 and 21473162). Y. Zhao is grateful to the Project Grants 521 Talents Cultivation of Zhejiang Sci-Tech University and China Scholarship Council (CSC) Foundation. This work is also supported by Zhejiang Provincial Top Key Academic Discipline of Chemical Engineering and Technology.

Author details

Yanying Zhao$^{1,2,*}$, Xin Liu$^1$ and Shuang Meng$^1$

*Address all correspondence to: yyzhao@zstu.edu.cn

1 Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, China

2 State Key Laboratory of Advanced Textiles Materials and Manufacture Technology, MOE, Zhejiang Sci-Tech University, Hangzhou, China

References


[14] Yang CT, Zhang ZQ, Liang J, Liu JH, Lu XY, Chen HH, Liu L. Copper-catalyzed cross-coupling of nonactivated secondary alkyl halides and tosylates with...


ethane, and halomethanes. Organometallics. 2009;28:1358–1368. DOI: 10.1021/om801077x


[27] Zhao Y. C–Cl activation by group IV metal oxides in solid argon matrices: matrix isolation infrared spectroscopy and theoretical investigations of the reactions of MOₓ (M = Ti, Zr; x = 1, 2) with CHₓCl₂. J. Phys. Chem. A. 2013;117(27):5664–5674.


[47] Zhao Y, Gong Y, Zhou M. Matrix isolation infrared spectroscopic and theoretical study of NgMO (Ng = Ar, Kr, Xe; M = Cr, Mn, Fe, Co, Ni) complexes. J. Phys. Chem. A. 2006;110(37):10777–10782. DOI: 10.1021/jp064100o
