CH$_2$I$_2$ adsorption and reactions on TiO$_2$

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Received 13th December 2002, Accepted 12th March 2003
First published as an Advance Article on the web 27th March 2003

Fourier-transform infrared spectroscopy has been employed to study the adsorption, thermal transformation, and photoreactions of CH$_2$I$_2$ on powdered TiO$_2$. At 35 °C, CH$_2$I$_2$ is adsorbed molecularly or dissociatively to form a surface species with CH$_2$I$_2$(a) and C–O functional groups possibly derived from C–I bond scission of CH$_2$I$_2$. As the surface temperature is raised above 100 °C, the adsorbed CH$_2$I$_2$ is transformed into CH$_4$O$_{1-3}$ and HCOO$_{1-3}$ simultaneously, very likely via disproportionation of the reaction intermediate of dioxymethylene (–OCH$_2$O–). Under UV irradiation in the presence of O$_2$, adsorbed CH$_2$I$_2$ on TiO$_2$ decomposes to form CO$_{1-3}$, HCOO$_{1-3}$, H$_2$O$_{1-3}$, and CO$_2$. But the CH$_2$I$_2$ photoreaction is almost terminated in the absence of O$_2$. The possible initiation species involved in the CH$_2$I$_2$ photodecomposition is discussed.

Introduction

Halogenated hydrocarbons are the compounds widely used in organic synthesis. Recently they are also used as precursors to generate hydrocarbon fragments on various metal or oxide-supported metal surfaces. Study of adsorbed hydrocarbon fragments is important to explore the mechanisms in heterogeneous catalytic synthesis. For instance, it has been believed that CH$_2$I$_2$ is a crucial surface intermediate for the formation of long chain hydrocarbons in Fischer–Tropsch synthesis. Adsorbed CH$_2$I$_2$ shows versatile surface reaction pathways, depending on the nature of the substrate. On Cu(100) surface, CH$_2$I$_2$ dissociates at 90 K at submonolayer coverage, whereas at monolayer the dissociation temperature raises to 192–240 K. CH$_2$(a) is produced on the surface after the C–I bond scission of CH$_2$I$_2$. Recombination of CH$_2$(a) generates C$_2$H$_4$(a) at temperature ~200 K. On Al(111), the surface reaction of submonolayer CH$_2$I$_2$ predominantly forms alkyl-aluminum complex of CH$_2$Al(H)$_{1-3}$(a) at 470 K. Upon increasing the coverage to one monolayer, C$_2$H$_4$(a) is generated at 150 K. The appearance of the alkyl-aluminum complex indicates that the role of the Al(111) is not just a surface medium providing a place for the recombination of adsorbed CH$_2$I$_2$. On Rh(111), the dissociation process of CH$_2$I$_2$ is similar to that on Cu(100); however, the CH$_2$(a) reacts to form CH$_4$(a) and C$_2$H$_4$(a). The evolution of CH$_4$ indicates that Rh is more reactive than Cu and leads to the dissociation of the C–H bond of CH$_2$I$_2$, providing the H source for the formation of C$_2$H$_4$(a). Interestingly, as the Rh(111) is preadsorbed with O atom, the C–I bond scission of CH$_2$I$_2$ is retarded and the CH$_2$(a) reacts with the adsorbed oxygen atoms to form C$_2$H$_4$O$_{1-3}$ between 170–340 K and CO$_2$(a) and H$_2$O$_{1-3}$ between 340–460 K. The route for the C$_2$H$_4$O$_{1-3}$ formation observed on clean Rh(111) is terminated. On Ag(111), no CH$_2$I$_2$ molecular desorption is detected at submonolayer coverages, and the thermal reaction product C$_2$H$_4$(a) is generated at 115, 135, or 230 K, depending on CH$_2$I$_2$ coverage. Infrared-spectroscopic study shows the formation of CH$_2$(a) as CH$_2$I$_2$(a) is heated to 155 K. In the presence of pre-adsorbed O on Ag(111), the formation of C$_2$H$_4$(a) decreases with increasing O coverage and CH$_2$I$_2$(a) becomes the main product at ~225 and 270 K instead. On Mo(100), CH$_2$I$_2$(a) is formed when CH$_2$I$_2$ adsorption layer is heated to 135 K and CH$_2$I$_2$(a) is generated at ~230 K.

On TiO$_2$, halogenated compounds have been extensively investigated under UV illumination. One of the major focuses of these studies is to destroy these hazardous compounds to innocuous species from the point of the view of environmental protection and amelioration. Irradiation of TiO$_2$ using photons with energy higher than its band gap generates conduction band electrons and valence band holes which may diffuse to the surface where they react with adsorbates and initiate photoreactions. Previously, we studied the adsorption and photoreactions of methyl iodide on TiO$_2$. The present study of CH$_2$I$_2$ is a continuation of our research project on halogenated C$_1$ and we investigate the adsorption, thermal reactions and photo-induced dissociation of CH$_2$I$_2$ on powdered TiO$_2$ by Fourier-transform infrared spectroscopy.

Experimental

The details of the stainless steel IR cell with two CaF$_2$ windows for IR transmission down to 1000 cm$^{-1}$ used in the present study have been reported previously. In our system, the IR cell was connected to a gas manifold which was pumped by a 60 L s$^{-1}$ turbomolecular pump with a base pressure of ~1 × 10$^{-7}$ Torr. The TiO$_2$ powder was supported on a tungsten grid (~6 cm$^2$). The preparation method has been described. In brief, TiO$_2$ powder (Degussa P25, ~50 m$^2$ g$^{-1}$, anatase 70%, rutile 30%) was dispersed in water-acetone solution to form a uniform mixture which was then sprayed onto a tungsten mesh. After that, the TiO$_2$ sample was mounted inside the IR cell for FTIR spectroscopy. The TiO$_2$ sample in the cell was heated to 450 °C under vacuum for 24 h by resistive heating. The temperature of TiO$_2$ sample was measured by a K-type thermocouple spotwelded on the tungsten mesh. Before each run of the experiment, the TiO$_2$ sample was heated to 450 °C in vacuum for 2 h. After the heating, 10 Torr O$_2$ was introduced into the cell as the sample was cooled to 70 °C. When the TiO$_2$ temperature reached 35 °C, the cell was evacuated for gas dosing. The TiO$_2$ sample after the annealing treatment still possessed residual surface hydroxyl groups. O$_2$ (99.998%) and CH$_2$I$_2$ (99%) were purchased from Matheson and Aldrich respectively. CH$_2$I$_2$ was purified by several cycles of freeze–pump–thaw before introduction to the cell. Pressure was monitored with a Baratron capacitance.
manometer and an ion gauge. In the photochemistry study, both the irradiation and IR beams were set 45° to the normal of the TiO$_2$ sample. The irradiation light source used was a combination of a 350 W–Hg arc lamp (Oriel Corp), a water filter, and a band pass filter with a band width of ~100 nm centered at 400 nm (Oriel 51670). The power at the position of TiO$_2$ sample was ~0.14 W cm$^{-2}$ measured in the air by a power meter (Molelectron, PM10V1). Infrared spectra were obtained with a 4 cm$^{-1}$ resolution by a Bruker FTIR spectrometer with a MCT detector. The entire optical path was purged with CO$_2$-free dry air. The spectra presented here have been ratioed against a clean TiO$_2$ spectrum providing the background reference.

Results

Fig. 1 shows the IR spectra of TiO$_2$ after being in contact with ~1.5 Torr of CH$_2$I$_2$ vapor at 35°C followed by evacuation at 35, 50, 100, 150, 200, 250, and 300°C for 1 min. In the 35°C spectrum, the bands at 1111, 1359, 2973, and 3058 cm$^{-1}$ are assigned to CH$_2$ twisting, scissoring, symmetric stretching, and antisymmetric stretching of adsorbed CH$_2$I$_2$, respectively, after comparing with the IR absorptions of CH$_2$I$_2$ in gas phase$^{16}$ and on Rh(111).$^{17}$ In addition, the band at 1226 cm$^{-1}$ is attributed to CH$_2$ wagging of the adsorbed CH$_2$I$_2$, since the gaseous CH$_2$Cl$_2$ wagging mode is at ~3600–3800 cm$^{-1}$ in the region of 3600–3800 cm$^{-1}$ assigned to CH$_2$ twisting, scissoring, symmetric stretching, and antisymmetric stretching based on the previous IR study of free CH$_2$I$_2$ (see Table 1). In spite of the –O–H bonding of –O–H ... I–CH$_2$I interaction, another interaction between CH$_2$I$_2$ and surface Ti$^{4+}$ Lewis acid site cannot be ignored. In Fig. 1, the amount of the surface CH$_2$I$_2$ decreases with increasing surface temperature. After shortly annealing to 300°C under vacuum, only ~15% residual CH$_2$I$_2$ is present on the surface and the broad band due to the hydrogen bonding are hardly detectable. However, the isolated OH bands are not recovered, because they are unstable at higher temperature. In the 35°C spectrum in Fig. 1, there are two bands at 1043 and 2877 cm$^{-1}$ that do not belong to CH$_2$I$_2$. They are characteristic frequencies for the stretching of C–O and CH$_x$, implying that CH$_2$I$_2$ may decompose on TiO$_2$ at 35°C and produce the surface species containing C–O and CH$_x$ functional groups. In the previous study of CH$_3$I adsorption on TiO$_2$, it has been shown that the C–I bond of the adsorbed CH$_3$I dissociates to form CH$_3$O(a) on the surface.$^{15}$ Scheme 1 shows three possible species responsible for the 1043 and 2877 cm$^{-1}$ because they possess C–O and CH$_x$ groups and are derived from C–I bond scission of CH$_2$I$_2$. In Fig. 1, as the surface temperature is increased higher than 100°C, new peaks appear at 1027, 1127, 1364, 1552, 2837, and 2937 cm$^{-1}$. Among them, the 1364 and 1552 cm$^{-1}$ bands are assigned to the COO symmetric and antisymmetric stretching of HCOO(a), which have been detected in formic acid dissociative adsorption on TiO$_2$. $^{23}$ The other four bands are attributed to CH$_2$I$_2$. The 1027 and 1127 cm$^{-1}$ are due to the C–O stretching and the 2837 and 2937 cm$^{-1}$ are due to the CH$_2$ symmetric and antisymmetric stretching based on the previous IR study of CH$_3$OH dissociative adsorption on TiO$_2$. $^{21,22}$ Note that the previous study has demonstrated that thermal decomposition of CH$_3$OH on TiO$_2$ in a vacuum does not generate HCOO(a).$^{23}$

Fig. 2 compares the reaction rates of adsorbed CH$_3$I and CH$_3$Br$_2$ on TiO$_2$ by holding the surface temperature at 55°C for 180 min in a closed cell to demonstrate the effect of the nature of carbon-halogen bond. In the 0 min spectrum of

<table>
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<tr>
<th>Table 1</th>
<th>Comparison of vibrational frequencies/cm$^{-1}$ of CH$_2$I$_2$</th>
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<tr>
<td>CH$_3$I$_2$</td>
<td>CH$_3$I$_2$/Rh(111)</td>
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<tr>
<td>(ref.16)</td>
<td>at 100 K (ref.17)</td>
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<td>3047</td>
<td>3030</td>
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<td>2968</td>
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<td>1353</td>
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<td>1106</td>
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CH$_2$Br$_2$, the bands located at 1192, 2987, and 3071 cm$^{-1}$ are assigned to CH$_2$ wagging and stretching of adsorbed CH$_2$Br$_2$. Assuming the same CH$_1$ stretching extinction coefficients for both adsorbed CH$_2$Br$_2$ and CH$_2$I$_2$, the initial adsorbed amount of CH$_2$I$_2$ at 35°C is estimated to be about twice that of adsorbed CH$_2$Br$_2$. In the case of CH$_2$I$_2$, HCOO(a) (1358 and 1551 cm$^{-1}$) and CH$_4$(a) (2831 and 2929 cm$^{-1}$) are produced after 180 min annealing at 55°C. If both the adsorbed CH$_2$Br$_2$ and CH$_2$I$_2$ have the same rate of thermal decomposition forming CH$_4$(a) and HCOO(a), the amounts of these two products derived from CH$_2$Br$_2$ and CH$_2$I$_2$ are expected to be about the same. The CH$_2$I$_2$-adsorbed and CH$_2$Br$_2$-adsorbed surfaces were prepared by exposing a clean TiO$_2$ surface to ~1.5 Torr of CH$_2$I$_2$ and CH$_2$Br$_2$, followed evacuation at 35°C. All of the spectra were measured at 35°C with 50 scans.

Fig. 2 shows the infrared spectra taken before and after holding the TiO$_2$ surface covered with CH$_2$I$_2$ (a) or CH$_2$Br$_2$ (b) at 55°C for 180 min. The four traces in the 2700-3200 cm$^{-1}$ region have been multiplied by a factor of two. The CH$_2$I$_2$-adsorbed and CH$_2$Br$_2$-adsorbed surfaces were prepared by exposing a clean TiO$_2$ surface to ~1.5 Torr of CH$_2$I$_2$ and CH$_2$Br$_2$, followed evacuation at 35°C. All of the spectra were measured at 35°C with 50 scans.

After 180 min photoirradiation, the CH$_2$I$_2$ bands, at 1111, 2973, and 3058 cm$^{-1}$, are only slightly reduced, accompanied with the formation of HCOO(a) at 1358 and 1551 cm$^{-1}$ and CH$_4$(a) at ~2830 and ~2930 cm$^{-1}$ which are hardly discernible in the scale used. Because the TiO$_2$ temperature is increased up to 55°C during the photoirradiation, the formation of HCOO(a) and CH$_4$(a) is not attributed to photodecomposition, but instead the thermal effect as demonstrated in Fig. 2. Fig. 4 shows the infrared spectra taken before and after the indicated times during UV exposure of CH$_2$I$_2$ adsorbed on TiO$_2$ surface in 10 Torr of O$_2$ in a closed cell. In contrast to the case of without O$_2$ in Fig. 3, the bands at 1111, 2973, and 3058 cm$^{-1}$ due to adsorbed CH$_2$I$_2$ are considerably reduced after 180 min irradiation, and thus leading to the enhanced bands at 1359, 1552, 1616, 2119, 2212, 2349, and 2874 cm$^{-1}$. The 1359 and 1552 cm$^{-1}$ are attributed to HCOO(a), 1616 to adsorbed H$_2$O, 2119 and 2212 cm$^{-1}$ to adsorbed CO, and 2349 to gaseous CO$_2$. It has been known that the fundamental frequencies of gaseous CO and HI are 2143 and 2230 cm$^{-1}$, respectively. Therefore the strong band at 2119 cm$^{-1}$ in Fig. 4 is attributed to adsorbed CO(a), instead of adsorbed HI. However, the possibility for the formation of HI in the CH$_2$I$_2$ photoreactions can not be completely ruled out. Furthermore, it is impossible in the present study to address the issues regarding the presence and the adsorption state of iodide produced from CH$_2$I$_2$ photodecomposition on TiO$_2$, because the vibrational frequencies of surface iodine is far below our detection limit of 1000 cm$^{-1}$. But the study of CH$_3$I decomposition on TiO$_2$ (110) surface has shown that I$_{(a)}$ is stable up to ~300°C as evidenced by X-ray photoelectron spectroscopy, however, it is desorbed from the surface above this temperature. The reaction pathway of CH$_2$I$_2$($s$) + HCOO($a$) + H$_2$O($a$) + CO($a$) + CO$_2$($g$) summarizes the products detected by our infrared spectrometer in the photodecomposition of CH$_2$I$_2$ on TiO$_2$. Recently, we have also studied the photoreactions of adsorbed CH$_2$I$_2$ and CH$_2$Br$_2$ on TiO$_2$ in the presence of $^{16}$O$_2$. Strong bands at 2127 cm$^{-1}$ in the CH$_2$I$_2$ case and at 2123 cm$^{-1}$ in the CH$_2$Br$_2$ case are observed and attributed to adsorbed CO. Furthermore, the photoreactions of CH$_2$I$_2$($a$) in the presence of $^{18}$O$_2$ produces two bands at 2077 and 2127 cm$^{-1}$ which
are attributed to C\textsuperscript{18}O(a) and C\textsuperscript{16}O(a) respectively.\textsuperscript{30} The relative amounts of CH\textsubscript{2}I\textsubscript{2}(a), HCOO(a), CO(a), and CO\textsubscript{2}(g) as a function of photoirradiation time are shown in Fig. 5. The amount of CH\textsubscript{2}I\textsubscript{2}(a) decreases with photoirradiation time and the decreasing rate is higher in the initial stage. The amounts of CO(a), HCOO(a) and CO\textsubscript{2}(g) increase monotonically. Since the CO(a) is produced as an intermediate, its increase with photoirradiation time shows the rate for its formation from CH\textsubscript{2}I\textsubscript{2} decomposition is higher than the rate for its consumption to form CO\textsubscript{2}(g). Since the surface temperature was increased to 55°C during the photoillumination of TiO\textsubscript{2}, a separate thermal control experiment was carried out by holding the CH\textsubscript{2}I\textsubscript{2}-adsorbed TiO\textsubscript{2} at 55°C in 10 Torr O\textsubscript{2} for 180 min without photon exposure. Fig. 6 compares the spectra of the TiO\textsubscript{2}, with the same initial amount of adsorbed CH\textsubscript{2}I\textsubscript{2} after photoreaction or surface heating at 55°C for 180 min. It is found that HCOO(a) is produced by the surface heating, however its amount is only ~50% of that produced by photoreaction. Furthermore, no CO(a) and CO\textsubscript{2}(g) are detected after the surface annealing at 55°C. Photoreaction of HCOO(a) on TiO\textsubscript{2} in the presence of O\textsubscript{2} has been investigated previously and CO\textsubscript{2}(g) is the only product observed from HCOO(a) photodecomposition.\textsuperscript{17} Therefore the CO(a) formation observed in Fig. 4 is not from HCOO(a) but instead directly from CH\textsubscript{2}I\textsubscript{2} photodecomposition in the presence of O\textsubscript{2}.

**Discussion**

In the present study, when a clean TiO\textsubscript{2} surface at 35°C is exposed to CH\textsubscript{2}I\textsubscript{2}, CH\textsubscript{2}I\textsubscript{2} adsorbed molecularly and can dissociate to form a surface species containing CH\textsubscript{x} and C–O functional groups. On TiO\textsubscript{2}, the adsorbed CH\textsubscript{2}I\textsubscript{2} and isolated surface OH groups forms hydrogen bonding. However the possible acid-base interaction between the lone pairs on the iodine atom of the adsorbed CH\textsubscript{2}I\textsubscript{2} and the Ti\textsuperscript{4+} surface Lewis acid sites can not be ruled out. This type of interaction between the oxygen lone pairs of C=O groups and Ti\textsuperscript{4+} ions on TiO\textsubscript{2} has been observed by the red-shift of the C=O stretching frequency.\textsuperscript{23} Due to the detection limit of our infrared spectrometer, it is impossible for us to detect the C\textsubscript{12}I\textsubscript{2} frequencies of the adsorbed CH\textsubscript{2}I\textsubscript{2}, but, the observed CH\textsubscript{2} frequencies are similar to those of gaseous CH\textsubscript{2}I\textsubscript{2}. In our previous adsorption study of CH\textsubscript{I} on TiO\textsubscript{2}, the C–I bond can dissociate at 35°C to form CH\textsubscript{3}O(a).\textsuperscript{12} In the present case of CH\textsubscript{2}I\textsubscript{2} on TiO\textsubscript{2}, the C–I bond dissociates as well, forming the surface species likely as shown in Scheme 1. The amount of adsorbed CH\textsubscript{2}I\textsubscript{2} decreases with increasing surface temperature under vacuum due to desorption and dissociation. CH\textsubscript{2}I\textsubscript{2} decomposes thermally on TiO\textsubscript{2} into CH\textsubscript{3}O(a) and HCOO(a) simultaneously. Based on the product distribution and bond energy difference between C–H and C–I, it is proposed that the CH\textsubscript{2}I\textsubscript{2} reaction is via dioxymethylene. Previously, Busca et al. investigated the thermal reactions of formaldehyde on TiO\textsubscript{2} by FTIR, they

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**Fig. 4** Infrared spectra taken before and after the indicated times during photoreaction of a TiO\textsubscript{2} surface covered with CH\textsubscript{2}I\textsubscript{2} in 10 Torr of O\textsubscript{2}. The CH\textsubscript{2}I\textsubscript{2}-adsorbed surface was prepared by exposing a clean TiO\textsubscript{2} surface to ~1.5 Torr of CH\textsubscript{2}I\textsubscript{2} followed evacuation at 35°C. All of the spectra were measured with five scans.

**Fig. 5** Relative concentrations of CH\textsubscript{2}I\textsubscript{2}(a), CO(a), CO\textsubscript{2}(g), and HCOO(a) as a function of photoirradiation time for the photoreactions of adsorbed CH\textsubscript{2}I\textsubscript{2} on TiO\textsubscript{2} in the presence of O\textsubscript{2}. The CH\textsubscript{2}I\textsubscript{2}-adsorbed TiO\textsubscript{2} surface was prepared by exposing a clean TiO\textsubscript{2} surface to ~1.5 Torr of CH\textsubscript{2}I\textsubscript{2} followed by evacuation at 35°C. The maximum amount of each species is scaled to 1.

**Fig. 6** Infrared spectra taken after 180 min photoirradiation (a) and surface heating at 55°C (b) for a TiO\textsubscript{2} surface covered with CH\textsubscript{2}I\textsubscript{2} in 10 Torr of O\textsubscript{2}. The surface was prepared by exposing a clean TiO\textsubscript{2} surface to ~1.5 Torr of CH\textsubscript{2}I\textsubscript{2} followed evacuation at 35°C. Both spectra were measured with five scans.
found the formation of dioxymethylenemethanol (–OCH₂O–) below 30°C, which decomposed via oxidation to form HCOO(CH₃) and H₂O via Cannizzaro-type disproportionation to form HCOO(CH₃) and CH₃OH concomitantly prior to 150°C. Furthermore, the difference in bond energies of C–H (~100 kcal mol⁻¹) and C–I (~55 kcal mol⁻¹) implies that the C–I bonds of the adsorbed CH₂I₂ on TiO₂ break preferentially thermodynamically, and are likely to form –OCH₂O–. This argument is also supported by the comparison of the decomposition of CH₃I₂ and CH₂Br₂ to form HCOO(CH₃) and CH₃OH on TiO₂ in Fig. 2. The adsorbed CH₂Br₂ has a smaller thermal reaction rate than that of CH₂I₂, since the C–Br bond energy is ~70 kcal mol⁻¹, ~15 kcal mol⁻¹ higher than that of C–I bond.

As TiO₂ absorbs photons with energy higher than its band gap, conducton band electrons and valence band holes are generated at the same time. They are original sources for the reduction and oxidation of adsorbates on TiO₂. In the present study of CH₂I₂ on TiO₂, CH₂I₂ photoreaction proceeds only in the presence of O₂, forming CO₂, HCOO(a), H₂O(a), and CO(a). The fact of no photoreaction for CH₂I₂ on TiO₂ in the absence of O₂ indicates that the photocemposition of adsorbed CH₂I₂ in O₂ is not due to direct photodissociation of adsorbed CH₂I₂. i.e. the photoreaction of CH₂I₂ on TiO₂ is mediated by TiO₂. In the previous studies of electrochemistry and electron dissociative attachment, CH₂Br₂ and CH₃Cl₂ were found to form transient molecular anions followed by dissociation into Br⁻ and CH₃Br⁺ for CH₂Br₂ and Cl⁻ and CH₃Cl⁺ for CH₃Cl₂.13,31 Therefore it is possible that the photoreaction of CH₂I₂ on TiO₂ is due to the photogenerated electrons in the conduction band. However, if this is the case, one would expect that the photoreaction rate of the adsorbed CH₂I₂ in the absence of O₂ is higher than that in the presence of O₂, because of the electron-scavenging property of O₂. Besides, based on the spectra in Fig. 3 taken during photolijmination of the adsorbed CH₂I₂ in the absence of O₂, except the slightly decreased CH₂I₂(a) bands and the enhanced HCOO(a) and CH₃O(a) bands due to the thermal effect, no new bands are observed. Therefore the conduction band electrons may not play important role in the photoinduced reaction of CH₂I₂ on TiO₂.

The photocemposition of the adsorbed CH₂I₂ to form CO₂, HCOO(a), H₂O(a), and CO(a) is an oxidative process. The possible species involved in the TiO₂-mediated photooxidation of CH₂I₂ are hole, OH⁺, and oxygen anions, such as O⁻, O₂⁻, O₃⁻, etc.10,11 The efficiency for hole capture by the CH₂I₂(a) depends on the match of the energy levels between CH₂I₂ occupied orbitals and TiO₂ valence band edge. OH⁺ radicals are possibly generated because the TiO₂ surface possesses isolated OH groups. On annealed TiO₂ surfaces upon UV irradiation at 77 K, ESR has shown the existence of O₂⁻, O₂⁻, O₃⁻ species.34 However only O₂⁻ is shown to be stable at room temperature. In the band gap irradiation of TiO₂ colloids suspended in aqueous solutions, ESR has shown also the trapped hole species to be oxygen surface anion radical covalently bound to titanium atoms.35 It has also been reported that CH₂Br₂ reacts with O⁻ or O₂⁻ in gas phase to produce Br⁻.36 The neutral species of Br, CH₃O or OBr are suggested to be formed in the reactions.36 In addition, theoretical calculations suggest that O⁻ involves in the photocemposition of CH₂I₂ and CH₃I on semiconductors.37,38 The exact species for the initiation of photooxidation of CH₂I₂ on TiO₂ is still under discussion.

Conclusion
As TiO₂ is exposed to CH₂I₂ at 35°C, CH₂I₂ is adsorbed moleculely or dissociatively to form a surface species with the structure as shown in Scheme 1 from C–I bond scission of CH₂I₂. The adsorbed CH₂I₂ is thermally transformed into CH₃O(a) and HCOO(a), probably via –OCH₂O–, and photo-

chemically transformed into CO₂(a), HCOO(a), H₂O(a), and CO(a) in the presence of O₂.

Acknowledgements
We gratefully acknowledge the financial support of the National Science Council of the Republic of China (Grant NSC 91-2113-M-006-012) for this research.

References