Study of Adsorption and Reactions of Methyl Iodide on TiO₂

C. Su,†,* J.-C. Yeh,† C.-C. Chen,† J.-C. Lin,‡,* and J.-L. Lin‡

*Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei, 106, Taiwan; and †Department of Chemistry, National Cheng Kung University, Tainan, 701, Taiwan

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The adsorption, thermal reactions, and photochemistry of methyl iodide were studied on powdered TiO₂ by transmission infrared spectroscopy, and on a TiO₂(110) single-crystal surface by temperature-programmed desorption (TPD) and X-ray photoemission spectroscopy (XPS). CH₃I is either adsorbed molecularly or adsorbed dissociatively, forming methoxy groups on powdered TiO₂ by thermal activation as observed by IR spectroscopy. The dissociation of CH₃I is enhanced by the presence of surface hydroxyl groups. CH₃I evolves thermally as a major product when CH₃I reacts with powdered TiO₂ in the absence of oxygen. However, only oxygen-containing reaction intermediates and products are found when oxygen is present, including CH₂O(g), (CH₃)₂O(g), CO(g), CO₂(g), and O₂(g). The formation of (CH₃)₂O(g) on TiO₂ occurs at much lower temperatures. It starts to evolve at ~200 K and reaches its maximum rate at 250–300 K depending on surface heterogeneity in the TPD study. The Williamson synthesis process is proposed for the generation of (CH₃)₂O(g) in this case. In addition, surface iodine formed by X-ray irradiation on CH₃I-covered TiO₂ is stable and is desorbed by 230 K. CH₃Cl is adsorbed molecularly on TiO₂(110) and is desorbed from the surface by 230 K. CH₃Cl also remains intact on powdered TiO₂ at 315 K. Here, we investigate the adsorption, thermal reactions, and photochemistry of CH₃I on powdered TiO₂. The C–I bond energy is ~30 kcal/mol lower than that of the C–Cl bond. It is intriguing to explore the possibility of breaking the C–I bond and follow the reaction pathways of the CH₃ group and iodine. Furthermore, because there are residual hydroxyl groups on the surface after our TiO₂ sample treatment, the effect of its presence on CH₃I dissociation is also studied. Recently, Garrett et al. have studied the adsorption and photochemistry on TiO₂(110) (12, 13). In the present work, the reaction of CH₃I on TiO₂(110) is studied for higher coverages that were not covered in Garrett’s paper and the results are compared to those obtained for powdered TiO₂. In addition, the photochemistry of CH₃I on powdered TiO₂ was studied in the absence of oxygen.

EXPERIMENTAL

The experiments were carried out in two separate vacuum systems to employ different techniques to study the reactions of CH₃I on powdered TiO₂ and on single-crystal TiO₂ surfaces, respectively. The system used for the powdered TiO₂ study and its IR cell have been described.
In the photoreaction study, both the IR beam and the irradiation light for inducing photochemistry were 45° to the normal of W-grid. The UV light source for the photochemistry study was constituted by a Hg arc lamp (350 W, Oriel Corp.), a water filter, and a band-pass filter (Oriel 51670) with a routine base pressure below 5 × 10⁻¹⁰ Torr. The pressure of the system was measured with a Baratron capacitance manometer and an ion gauge. The powdered TiO₂ used in the study was supported on a tungsten grid of ~6 cm². This grid was held in a pair of stainless steel clamps which were attached to the power leads of a power/thermocouple feedthrough. The sample temperature was measured by a K-type thermocouple spot-welded on the top of the W-grid. Samples were made by spraying onto the W-grid a slurry of TiO₂ powder (Degussa P25, ~50 m²/g, anatase ~70% and rutile ~30%) dispersed in a mixture of water and acetone. The TiO₂ sample was then mounted into the IR cell for in situ monitoring of the reaction process by Fourier transform infrared spectroscopy (FTIR) and thoroughly outgassed at 723 K for 24 h under vacuum. Before each run of the experiment, the TiO₂ sample was heated to 723 K for 2 h. When the sample was cooled to 343 K after the heating, 10 Torr of O₂ was introduced into the cell while the sample’s temperature decreased continuously. As the temperature reached 308 K, the cell was evacuated for gas dosing. This procedure caused surface dehydration and removed adsorbed hydrocarbons, but a small amount of residual hydroxyl groups still existed. This surface was also highly defective, resulting from inherent poorly organized surface atoms on powder particles and from the surface annealing process in vacuum. For prolonged annealing at 723 K in vacuum, the TiO₂ powder sometimes turned a light gray color.

In the photoreaction study, both the IR beam and the irradiation light for inducing photochemistry were 45° to the normal of W-grid. The UV light source for the photochemistry study was constituted by a Hg arc lamp (350 W, Oriel Corp.), a water filter, and a band-pass filter (Oriel 51670) with ~100 nm bandwidth centered at ~400 nm. The power at the position of the TiO₂ sample was ~0.14 W/cm² measured in the air by a power meter (M eenor, PM 10V 1). Infrared spectra were obtained with 4 cm⁻¹ resolution by a Bruker Fourier transform infrared spectrometer with an MCT detector. The entire optical path was purged with CO₂-free dry air. Each spectrum presented in this paper has been ratioed against clean TiO₂ spectra.

The reactions of CH₃I on the TiO₂ (110) surface were investigated in a two-level ultrahigh vacuum (UHV) system with a routine base pressure below 5 × 10⁻¹⁰ Torr. A detailed description of the system design has been given previously (16). Briefly, the chamber was equipped with a four-grid reverse viewing low-energy electron diffraction (LEED) optics (VG, RVL-900) for surface structure determination, an Auger electron spectrometer (AES) for surface elemental analysis, an ion sputtering gun (PHI 04-177) for TiO₂ (110) surface cleaning, and a quadrupole mass spectrometer (OMS) (UTI, 0-300 amu) for temperature-programmed desorption experiments. The QMS was situated in a copper tube and separated from the main chamber by a Mo cone with a 2-mm-diameter aperture, and differentially pumped with two small ion pumps (20 L s⁻¹).

The TiO₂ (110) single crystal (10 mm × 10 mm × 1 mm) used in this study was obtained from Commercial Crystal Laboratories Inc. The crystal was first treated by ultrasonic cleaning in acetone and methanol solvents to remove organic contaminants on the surface and then was fastened to a 1-mm-thick tantalum (Ta) supporting plate with a gold foil placed in between for intimate thermal contact (17). Two Ta wires (0.5 mm diameter) were spot-welded on the back side of the Ta supporting plate and connected to the power feedthrough. Variation of the temperature of the TiO₂ sample assembly was achieved by a combination of liquid-nitrogen cooling and resistive heating via the Ta wires.

The TiO₂ (110) surface temperature was monitored by a K-type thermocouple spot-welded onto a tiny bend-over Ta tab which was inserted into a precut slot at one of the corners of the crystal as shown in Fig. 1. Computer software was employed to linearly control the TiO₂ temperature between 100 and 1000 K and to record multiple QMS signals simultaneously for TPD study.

The TiO₂ crystal was cleaned by Ar⁺ ion bombardment (500 eV, 10 min, current ~2 μA). Surface cleanliness was frequently checked by AES. The surface stoichiometry was achieved by annealing the cleaned surface at 1000 K for 3 min in 2 × 10⁻⁶ Torr of O₂ followed by cooling to room temperature (10 min) at the same oxygen pressure. The crystal color changed from transparent to dark blue after heating of the crystal to 1000 K under vacuum. This surface is also called a “smoothed surface” hereafter in the following TPD study. After the treatment, a (1 × 1) LEED pattern with sharp diffraction spots was obtained. XPS showed sharp Ti 2p peaks with no obvious indication of a reduced Ti state. There were fully coordinated and five-fold-coordinated Ti⁺⁺⁺ cations present on this surface.

![FIG. 1. Schematic showing the design of the sample holder for the TiO₂ (110) single crystal.](image-url)
However, there might also exist, even in a small amount, surface defect sites, such as lattice oxygen vacancy, single bridging oxygen vacancy, and double bridging oxygen vacancy (18). Note that there were no surface hydroxyl groups on this single-crystal surface after the cleaning and annealing treatment. The previous study by Pan et al. (19) has shown that annealing TiO\(_2\) in a vacuum or sputtering the surface causes a slightly oxygen-deficient or highly oxygen-deficient TiO\(_2\)(110) surface, respectively. Due to the loss of the surface oxygen atoms, there are several Ti reduced states present on the surface as observed by XPS (19). The sputtered surface also loses the long-range order as suggested by the appearance of vague LEED image.

Methyl iodide (99.5%, Aldrich), shielded from light, was purified by several cycles of freeze–pump–thaw before introduction into the IR cell or the UHV chamber. The O\(_2\) gas used was purchased from Matheson with 99.998% purity.

**RESULTS**

A**dsorption of CH\(_3\)I and Formation of CH\(_3\)O on Powdered TiO\(_2\)**

Figure 2a shows the infrared spectrum of TiO\(_2\) at 308 K in contact with 2 Torr of CH\(_3\)I. Below 3100 cm\(^{-1}\), absorption bands appear at 1245, 1261, 2832, 2927, 2955, and 2980, and 3050 cm\(^{-1}\). Above 3100 cm\(^{-1}\), a broad band centered at \(\sim 3535\) cm\(^{-1}\) and negative bands in the region of 3600–3750 cm\(^{-1}\) are observed. Since CH\(_3\)I is present in the gas phase of the reaction system, it is expected that its absorption bands appear in Fig. 2a. To locate their positions, a CH\(_3\)I gaseous infrared spectrum (Fig. 2b) was obtained in a separate experiment using the same optical operating condition as those for Fig. 2a. Four major bands at 1240, 1261, 2959, and 2980 cm\(^{-1}\) are observed. By comparing the band frequencies and their relative intensities for Figs. 2a and 2b, it is concluded that the bands of 1245, 2832, 2927, 2955, and 3050 cm\(^{-1}\) in Fig. 2a are not due to CH\(_3\)I in the gas phase.

In the previous study of TiO\(_2\) at 315 K in contact with CH\(_3\)Cl, Wong et al. observed that the adsorbed CH\(_3\)Cl exhibits infrared absorptions at 1236, 1444, and 2964 cm\(^{-1}\) (11). Based on Wong’s result, the bands at 1245, 2955, and 3050 cm\(^{-1}\) in Fig. 2a are thus attributed to CH\(_3\)I absorbed on the TiO\(_2\).

These absorption frequencies are assigned to CH\(_3\)I symmetric deformation, symmetric stretch, and antisymmetric stretch, respectively (20). When the reaction system of TiO\(_2\) in 2 Torr of CH\(_3\)I was evacuated, it is found that absorption bands due CH\(_3\)I either in the gas phase or on the surface disappear. It is worth noting that the bands of 1245, 2955, and 3050 cm\(^{-1}\) are not due to CH\(_3\)I in a multilayer, but instead due to CH\(_3\)I directly bonded to the TiO\(_2\) surface. This conclusion is based on two reasons. In the previous TiO\(_2\)(110) TPD study, Garrett et al. observed that CH\(_3\)I is desorbed from multilayer by 220 K (12, 13). In addition, in terms of the relationship of temperature–pressure for the CH\(_3\)I vapor–liquid equilibrium system (21), the temperature needed to condense 2 Torr of CH\(_3\)I into a multilayer liquid phase is much lower than 308 K. Furthermore, although the band at 2832 cm\(^{-1}\) may also be assigned to the overtone of TiO\(_2\) antisymmetric deformation (20), the simultaneous presence of 2832 and 2927 cm\(^{-1}\) indicates the formation of methoxy groups on TiO\(_2\). The identification of adsorbed methoxy groups (CH\(_3\)O\(_a\)) from dissociative CH\(_3\)OH adsorption on TiO\(_2\) by infrared spectroscopy has been reported previously (22–25). The negative bands at 3600–3750 cm\(^{-1}\) show the decrease of surface hydroxyl groups on TiO\(_2\) after the adsorption of CH\(_3\)I. This reduction may be partly due to H-bonding of the hydroxyl groups with the adsorbed CH\(_3\)I, as supported by the appearance of the broad feature centered at \(\sim 3535\) cm\(^{-1}\). Figure 2c shows the spectrum taken at 343 K after the TiO\(_2\) initially in 2 Torr of CH\(_3\)I was heated to 343 K and maintained at this temperature for 90 min. Several changes of adsorption features occur due to this TiO\(_2\) annealing treatment. First, the peaks due to methoxy groups grow with the surface annealing and shift slightly to higher frequencies of 2835 and 2935 cm\(^{-1}\).

Second, the diminishing band intensities of adsorbed CH\(_3\)I indicate that its adsorbed amount decreases with increasing surface temperature and this is in part due to the possible site-blocking effect of adsorbed methoxy groups and in part due to thermal desorption. Third, because of the changes...
in surface adsorption as mentioned above, the absorption features in the hydroxyl stretching region are also affected. The broad feature at ~3535 cm⁻¹ almost disappears, accompanied with a new absorption at 3637 cm⁻¹. This reflects the changes in the hydroxyl local bonding environment. Since in our TiO₂ sample preparation process, surface hydroxyl groups cannot be completely removed, the effect of the surface hydroxyl groups on the CH₃I adsorption and reaction on TiO₂ was therefore further studied. To prepare a hydroxylated TiO₂ surface, a clean TiO₂ surface was exposed to 1 Torr of H₂O vapor at 308 K, followed by annealing at 423 K for 1 min and evacuating at 443 K for 5 min to remove adsorbed water (26). Figure 2d shows the infrared spectrum for the hydroxylated TiO₂ in contact with 2 Torr of CH₃I at 308 K. Below 3100 cm⁻¹, the infrared absorption features are similar to those in Fig. 2a, except that the intensities of 1245 and 2955 cm⁻¹ from adsorbed CH₃I are ~10% less. A broad 3000 cm⁻¹ feature, situated on a broad adsorption feature extended from ~3000 to 3750 cm⁻¹, appear at 3418, 3649, 3675, and 3724 cm⁻¹. Previously, IR band assignments for TiO₂ surface hydroxyl groups have been reported in the literature (26–31). Primet et al. have found that surface hydroxyl groups absorb at 3410, 3655, and 3685 cm⁻¹ on rutile TiO₂ as well as at 3665 and 3715 cm⁻¹ on anatase TiO₂. The 3685 and 3715 cm⁻¹ bands are assumed to be isolated hydroxyls and the others are reasoned to result from hydroxyl groups bonded to each other by hydrogen bridges (27). However, Tanaka and White have assigned the bands at 3676 and 3715 cm⁻¹ on anatase TiO₂ to isolated hydroxyls bonded to Ti ions with different coordination or on different anatase faces (26). In terms of the Tanaka assumption, the lower amount of adsorbed CH₃I on hydroxylated TiO₂ as observed in Fig. 2d is probably related to the hydroxyl site-blocking effect. Very likely, CH₃I is interacting via the lone pair electrons on the iodine atom with the Ti ions on TiO₂. Therefore, the amount of CH₃I adsorption is reduced by the presence of hydroxyl groups occupying the Ti ions sites. Figure 2e shows the spectrum taken at 343 K after the hydroxylated TiO₂ initially in 2 Torr of CH₃I at 308 K was heated to 343 K and kept at this temperature for 90 min. The bands at 2832 and 2930 cm⁻¹ from methoxy groups increase in intensity with the surface annealing treatment at 343 K. However, due to the surface hydroxylation, its amount is twice that in Fig. 2c. Meanwhile, the isolated hydroxyl peaks at 3675 and 3724 cm⁻¹ disappear, whereas the 3418 and 3649 cm⁻¹ peaks of the hydroxyl groups involving in hydrogen bonding remain unchanged. This indicates that the latter types of hydroxyl groups lack reactivity toward CH₃I.

Thermal Reactions of CH₃I on Powdered TiO₂

Figure 3 shows the infrared spectra taken at the indicated temperatures during linear heating of the TiO₂ sample at a rate of 2 K/s (from 308 to 673 K) in the presence of ~20 Torr of CH₃I. The spectrum recorded at 433 K resembles the one for gaseous CH₃I. The absorptions due to adsorbed CH₃I are not obvious in this spectrum, because a lower amount of TiO₂ was used in this experiment and its absorptions may be buried in the large absorption bands of CH₃I in the gas phase. Following thermal activation, peaks appears at 1307 (not shown) and 3017 cm⁻¹, revealing the formation of methane in the gas phase (32). Methane starts to evolve at ~623 K and is the major product detected. A small amount of CO₂ is also observed at 2349 cm⁻¹. When oxygen is present in the reaction system, the reaction pathways are completely different. Figure 4 shows the infrared spectra recorded at the indicated temperatures during heating of the TiO₂ at a rate of 2 K/s up to 673 K in the presence of a mixture of ~25 Torr of CH₃I and ~70 Torr of O₂. No methane is detected in the reaction system throughout the heating process. Instead, only partially oxidized intermediates and fully oxidized products are observed, including dimethyl ether ((CH₃)₂O (g), 1178 cm⁻¹), formaldehyde (CH₂O (g), 1745 cm⁻¹), carbon monoxide (CO (g), 2143 cm⁻¹), carbon dioxide (CO₂ (g), 2349 cm⁻¹), and water (H₂O (g), 1653 cm⁻¹) (32). The relative concentrations of water, carbon monoxide, carbon dioxide, formaldehyde, dimethyl ether, and unreacted methyl iodide as a function of TiO₂ temperatures are plotted in Fig. 5a. Formation of the oxygen-containing compounds and their temperature-dependent behavior are similar to those of methanol interacting with TiO₂. In the methanol case, previous studies have shown that these compounds are due to the reaction of adsorbed methoxy groups with TiO₂ surfaces (23, 33–36). This similarity in the reaction
Variation of the IR spectrum of the TiO$_2$, initially in contact with a mixture of ~25 Torr of CH$_3$I and ~70 Torr of O$_2$ at 308 K, with temperature. (a and b) Spectra taken at 433 and 663 K, respectively, while the TiO$_2$ sample was linearly heated to 673 K at 2 K/s. (c) Spectrum taken after the TiO$_2$ temperature was held at 673 K for 40 s. All of the spectra were recorded with five scans. The TiO$_2$ sample used was ~30 mg.

pathways and reaction kinetics suggests the same reaction-initiating surface intermediate, i.e., CH$_3$O(a), is formed in the present study of CH$_3$I interacting with TiO$_2$. This argument is consistent with the result shown in Fig. 2, which indicates the formation of methoxy species due to CH$_3$I decomposition. Figure 5b shows the continuing changes of the gaseous compounds as a function of time as the TiO$_2$ sample is held at 673 K. While CH$_3$I declines continuously, CH$_2$O$_2$(g) and (CH$_3$)$_2$O$_2$(g) keep increasing, reaching their maxima at ~30 and ~80 s, respectively and then decrease slowly. CO(g) also shows a maximum at ~300 s and decreases slightly upon further annealing, presumably due to oxidation to monotonically increased CO$_2$(g). H$_2$O(g) reaches its maximum at ~80 s and gradually decreases up to ~380 s, and then becomes almost constant. This decrease in the period of 80-380 s proceeds concurrently with the increase of surface hydroxyl groups as observed by IR spectroscopy in the range of 3600-3800 cm$^{-1}$ (not shown).

Photooxidation of CH$_3$I on Powdered TiO$_2$

The photochemistry of CH$_3$I over powdered TiO$_2$ was studied in the absence and in the presence of O$_2$. Figure 6a shows the spectrum for the TiO$_2$ at 308 K in contact with a mixture of 2 Torr of CH$_3$I and 10 Torr of O$_2$. After 3 h of photoillumination, CO$_2$(g) and surface formate groups (HCOO$_{(a)}$, 1360, 1381, 1551, and 2870 cm$^{-1}$) (25, 37) are observed as shown in Fig. 6b. From the differential spectrum shown in Fig. 6c, the surface amount of adsorbed CH$_3$I (1245 and 2955 cm$^{-1}$) is considerably decreased. This decrease may be due to a combination effect of formate site blocking, surface heating upon the UV irradiation, and consumption by photoreaction. Because the TiO$_2$ surface temperature was raised to ~330 K upon UV irradiation, a thermal control experiment was carried out as well. In this experiment, the TiO$_2$ was exposed to a mixture of 2 Torr of CH$_3$I and 10 Torr of O$_2$, and the IR spectrum was then monitored as a function of time while the TiO$_2$ sample was held at this temperature. It was found that the formation of formate groups was negligible after 3 h of annealing at 330 K. Furthermore, since methoxy groups are generated after CH$_3$I dissociative adsorption on the TiO$_2$ surface, the role of methoxy groups in the photooxidation was also investigated. A methoxy-covered TiO$_2$ surface was prepared by exposing a clean TiO$_2$ to 2 Torr of methanol followed by evacuation at 523 K for 1 min (23–25). Figure 6d shows the spectrum of this methoxy-covered TiO$_2$ sample at 308 K in contact with 10 Torr of O$_2$. Figure 6e shows the results

![Graph](image_url)
of the photochemistry of the surface methoxy groups in the presence of $O_2$. It is found that in addition to formate formation, surface water ($H_2O_{(a)}$, 1620 cm$^{-1}$) is concomitantly formed during the irradiation. A similar observation has been reported for methoxy groups irradiated at 320 nm in the presence of $O_2$ (24). The major difference between the photochemistry of methoxy groups and CH$_3$I is the relative concentration of surface water to formate formed. This value is much higher for methoxy groups, indicating that the major contribution for the formate formation in the photooxidation of CH$_3$I over TiO$_2$ is not from adsorbed methoxy groups. The possible intermediate to initiate the surface photochemistry of CH$_3$I on TiO$_2$ will be discussed in the next section. On the other hand, in the study of photolillumination of the TiO$_2$ sample in 2 Torr of CH$_3$I in the absence of $O_2$, although the high-frequency end of the light source used in this experiment may decompose CH$_3$I, however, probably due to slow reaction rate, no gaseous or surface species other than CH$_3$I and surface methoxy groups are detected after 2 h of illumination.

Temperature-Programmed Desorption Study of CH$_3$I on TiO$_2$(110)

The adsorption and photochemistry of methyl iodide on TiO$_2$(110) have been reported recently by Garrett et al. (12, 13). In their TPD study, methyl iodide is desorbed with complex behavior due to the presence of surface defects and repulsive lateral interactions between the adsorbed molecules. At low coverages, methyl iodide is adsorbed more strongly at the defect sites and is desorbed at $\sim 210$ K. Increasing the coverage, the methyl iodide desorption peak shifts to lower temperatures, reaching $\sim 150$ K at one monolayer. The multilayer CH$_3$I is desorbed with peaks at 130-145 K. Similar methyl iodide molecular desorption is observed in the present study and therefore no TPD results are intended to be presented here. In our study, a exposure of $\sim 2.4$ l corresponds to 1 ML. In addition to the molecular desorption, an extensive mass search was performed for higher CH$_3$I coverages in the TPD study to identify other possible desorption products. Figure 7 shows the TiO$_2$(110) TPD spectra of dimethyl ether represented by the m/e = 45 ion at the indicated exposures for a smoothed surface and a sputtered surface (prepared by Ar$^+$ bombardment at 500 eV, 2 $\mu$A, and 300 K). The dimethyl ether evolution is identified by comparing the fragmentation pattern obtained from the integrated TPD peak area at the masses of 29, 30, 45, and 46 amu to the standard mass spectrum (38). Dimethyl ether shows a single desorption peak, for all of the exposures in Fig. 7, with lower peak temperatures at higher CH$_3$I exposures. Note that formation of dimethyl ether occurs only at multilayer coverages. Since the methyl

![FIG. 6. IR spectra of TiO$_2$ in contact with a mixture of 2 Torr CH$_3$I and 10 Torr $O_2$ before irradiation (a) and after 180 min of irradiation (b). The TiO$_2$ sample used was $\sim 35$ mg. (c) Net spectrum obtained by subtracting (b) from (a). (d and e) Spectra of methoxy-covered TiO$_2$ before irradiation and after 150 min of irradiation in 10 Torr of O$_2$, respectively. The TiO$_2$ sample used was $\sim 30$ mg. The methoxy-covered TiO$_2$ surface was prepared by exposing clean TiO$_2$ to 2 Torr of methanol followed by evacuation at 523 K for 1 min. All the traces in the range of 2800–3100 cm$^{-1}$ are multiplied by 2 and those in the range of 2050–2450 cm$^{-1}$ are multiplied by 3. All of the spectra were taken with five scans.

![FIG. 7. Temperature-programmed desorption spectra of dimethyl ether represented by the m/e = 45 ion at the indicated CH$_3$I exposures for a smoothed (upper panel) and a sputtered (lower panel) TiO$_2$(110) surface.]
iodide is completely desorbed from the surface by 250 K, the evolution of dimethyl ether is very likely limited by its desorption step. Compared to the case of the smoothed surface, the TPD peaks from the sputtered surface are much broader and shifted to higher temperatures, reflecting the effect of surface site heterogeneity and higher desorption energy for dimethyl ether from the sputtered TiO$_2$(110) surface. No iodine-containing products were detected within our QMS detection limit in TPD experiments.

XPS has been used complementarily to monitor the surface species for the TiO$_2$ surface which was previously exposed to 150 l of methyl iodide at 115 K followed by linear heating to 350 K. No carbon- or iodine-containing species on the surface are detected after the heating other than titanium and oxygen. This result indicates that either all the C and I have been desorbed from the surface by 350 K or the amount of CH$_3$I reacting with the surface is so small that the surface species resulting from CH$_3$I decomposition cannot be detected by our X-ray photoemission spectrometer. The previous study by Garrett et al. has shown that the I(3d$_{5/2}$) core level photoemission peak for molecularly adsorbed methyl iodide on TiO$_2$(110) is at 620.2 eV, while that of the adsorbed iodine produced by UV irradiation of the adsorbed methyl iodide is at 618.7 eV (12, 13). Since the thermal reactions as shown in the present study are induced by C–I bond dissociation of adsorbed methyl iodide, iodine atoms would have to be left on the surface. Therefore, its stability with respect to temperature was further studied by XPS for the sputtered TiO$_2$(110) surface. It has been reported that X-ray irradiation is able to induce chemical change in the methyl iodide layer adsorbed on TiO$_2$(110) (13). Accordingly, a similar procedure was followed in the present study to dissociate the adsorbed methyl iodide layer to generate surface iodine. Figure 8 shows the change of the I(3d$_{5/2}$) photoemission peak for the sputtered TiO$_2$ surface previously exposed to 8 l of methyl iodide at 105 K followed by X-ray irradiation for 20 min and flashing to the indicated temperatures. For the trace at 115 K, the peak is located at 621.4 eV which is attributed to the remaining adsorbed methyl iodide (CH$_3$I(a)) after X-ray irradiation and a small surface temperature increase. After heating to 253 K to desorb the remaining CH$_3$I(a), a peak at 619.8 eV, albeit small, is clearly observed. Compared to the previous assignment for the surface iodine photoemission, this peak is attributed to the adsorbed iodine (I(_a)) (12, 13). It can be completely desorbed from the surface by 570 K. The slight differences in the binding energies for CH$_3$I(a) and I(_a) observed here and those in Garrett’s work could be due to the spectrometer work function calibration.

**DISCUSSION**

From the IR study, CH$_3$I is adsorbed on powdered TiO$_2$ in two different forms. One is reversibly adsorbed molecular CH$_3$I. The other one is methoxy groups from CH$_3$I decomposition. In the absence of oxygen, the methoxy groups further dissociate to generate methane as a major thermal product. In the presence of oxygen, CH$_2$O$_2$(g), (CH$_3$)$_2$O(g), CO(g), CO$_2$(g), and H$_2$O(g) are produced and the channel for the formation of methane is terminated. In the previous study of alcohol reactions on TiO$_2$, Barteau et al. have proposed different reaction pathways for the gaseous reaction products (34, 35, 39). It is suggested that CH$_4$ formation from methoxy decomposition is initiated by C–O bond scission to fill surface oxygen vacancies, forming CH$_3$ species. A portion of these methyl groups may dissociate to generate surface hydrogen which instantaneously reacts with the remaining methyl groups to form methane. Presumably, when oxygen is present in the gas phase and the surface oxygen vacancies are effectively filled with dissociatively adsorbed O$_2$, the methane production channel is terminated. In this case, surface methoxy groups would follow another pathway to form oxygen-containing compounds. It may dehydrogenate to form formaldehyde which reacts with TiO$_2$ surfaces to produce adsorbed formate (37). Decomposition of the formate groups results in the formation/desorption of carbon monoxide and carbon dioxide from the surfaces (34–36). Dimethyl ether is the reaction product from coupling of two adsorbed methoxy groups (34, 39). In the present study, formation of dimethyl ether was also found in the TPD study of CH$_3$I adsorbed on a single-crystal TiO$_2$(110) surface, but it occurs only at multilayer coverages. If the mechanism for the formation of dimethyl ether on TiO$_2$(110) is same as that on powdered TiO$_2$, dimethyl ether is expected to be observed at monolayer coverage. However, this is not the case, implying another reaction mechanism must exist. Furthermore, the formation temperature of (CH$_3$)$_2$O on TiO$_2$(110) is much lower than that on powdered TiO$_2$. Two possibilities, for the (CH$_3$)$_2$O yield that appears to scale
with multilayer exposure, due to CH$_3$I contamination with (CH$_3$)$_2$O or electron-induced reaction during TPD study have been ruled out. It was found that no cracking pattern for (CH$_3$)$_2$O was observed by our mass spectrometer at 10$^{-6}$ Torr of CH$_3$I backing pressure and that similar results were obtained in the TPD study of CH$_3$I on TiO$_2$ with a negative sample bias at −65 V to repel possible strayed electrons emitting from our mass spectrometer operated at −55 V bias at electron source (filaments). There is a well-known reaction in the condensed phase called “Williamson synthesis” in which alkoxide ions attack alkyl halides to form ether (40). Therefore, it is postulated that on single-crystal TiO$_2$(110), methoxide ions may be produced by simultaneously breaking CH$_3$I and Ti-O bonds and forming a CH$_3$O bond and then migrating into the CH$_3$I multilayer where they nucleophilically attack CH$_3$I, generating dimethyl ether which subsequently diffuses back to adsorb directly at the TiO$_2$ surface. The following desorption of dimethyl ether from TiO$_2$ is the rate-limiting step for its evolution in the TPD study and depends on the surface heterogeneity as observed in Fig. 7. In the present study, the presence of a multilayer may induce the surface reaction by promoting the dissociation of adsorbate molecules in the monolayer. Recently, in the study of activation of cyclobutane on Ru(001), Hagedorn et al. have reported multilayer-assisted decomposition of the adsorbates in the monolayer at a temperature at which the monolayer would not dissociate without the multilayer (41). The electron-induced chemical reaction on alkyl halide films, though it has been reported by White et al. (42), is unlikely in our experiment. The formation of dimethyl ether was also observed with sample negatively biased to the mass spectrometer to prevent electrons from reaching the surface.

Since all of the reactions on TiO$_2$ surfaces are initiated by decomposition of CH$_3$I, more specifically speaking, by C–I bond dissociation to produce methoxy species, we discuss here the mechanism for CH$_3$I decomposition in this study by comparing the previously proposed mechanisms for the formation of methoxy groups from other precursors, molecules, such as CH$_3$OH and CH$_3$Cl, on various oxidic surfaces. In the case of methanol decomposition forming methoxy groups on TiO$_2$, in previous studies two origins have been proposed (34, 36, 39). Methanol may react with surface hydroxyl groups to form methoxy and water. This reaction pathway has been shown to be suppressed as TiO$_2$ sample is pretreated at 673 K to largely remove surface hydroxyl groups. In the previous study of CH$_3$Cl dissociation on a thin layer of alumina, Beebe et al. have found that surface hydroxyl groups are consumed, accompanied with the formation of surface methoxy groups (43). These data implicate the involvement of surface hydroxyl groups in the C–Cl bond dissociation as well as in the methoxy formation. The other channel for the formation of methoxy species may occur at coordinatively unsaturated TiO$_2$ cations through dehydrogenation of methanol by neighboring surface oxygens. Dissociative adsorption of methanol without involvement of surface hydroxyl groups has also been observed on mangesium oxide (44), germanium oxide (45), silicon oxide (46, 47), and aluminum oxide (48). Hence, the surface hydroxyl groups play an important role in the C–I bond breakage for the enhanced formation of methoxy groups as shown in Fig. 2. This enhancement occurs at the expense of hydroxyl groups only at 3675 and 3724 cm$^{-1}$. It is interesting to find that only certain types of OH groups assist the CH$_3$I decomposition, probably via nucleophilic attack of basic hydroxyl groups. Primet et al. have shown the basic character for the hydroxyl groups on anatase and rutile TiO$_2$ by using CO$_2$ as probing molecules (49). In addition, Che et al. have detected TCNE$^-$ and TNB$^-$ radical ions during the adsorption of tetracyanoethylene and trinitrobenzene on anatase TiO$_2$ which are attributed to the presence of OH$^-$ groups on the surface (50). The difference in thermal reactivity for CH$_3$I on powdered TiO$_2$ and on single-crystal TiO$_2$ surfaces can be attributed to the presence of various crystallographic facets, defects, and hydroxyl groups on the former surface. For photochemistry of CH$_3$I over powdered TiO$_2$, no spectroscopic evidence shows that CH$_3$I photoreaction takes place in the absence of O$_2$. In contrast, as O$_2$ is present, formate and CO$_2$(g) are formed as major products. Previous studies have shown that CO$_2$(g) is derived from photooxidation of formate groups (51, 52). Wong et al. have studied the photooxidation of CH$_3$Cl on powdered TiO$_2$ in the presence of O$_2$ using the full wavelength emitted from a 350-W Hg arc lamp (11). They have proposed a radical-mediated mechanism, initiated by superoxide, O$_2^-$, from the combination of photoelectrons and absorbed oxygen on the TiO$_2$ surface, to explain the formation of CH$_2$Cl$_2$. It is believed that the photoreactions in the present study may also be initiated by superoxide, O$_2^-$. Because it has been reported that on TiO$_2$ surfaces upon UV irradiation at 77 K, EPR (electron paramagnetic resonance) shows the existence of O$_2^-$, O$_3^-$, and O$_2$ species and only the last one is shown to be stable at room temperature (53). In the present study of CH$_3$I photochemistry on powdered TiO$_2$ in O$_2$ to form formate, since no kinetically short-lived intermediates are detected, no detailed reaction pathways are presented here. However, the related results from previous studies may provide insights into the formate formation. Jenkin
et al. have found the formation of CH$_3$O and HCOOH during the reaction of CH$_3$O radicals and O$_2$ in the gas phase (54). If CH$_3$O radicals are formed near the TiO$_2$ surface from the interaction of CH$_3$I with O$_2$ on the single crystal at multilayer coverages. On the other hand, it may be due to “Williamson synthesis” and CH$_3$I decomposes on this surface to form CH$_3$O(a). Its dissociation rate is different, indicating different operative mechanisms. On the powdered surface, it comes from coupling of two CH$_3$O(a). It makes a link to the solid–liquid interaction (41). In the TPD study, (CH$_3$)$_2$O is also found to be the desorption product. (CH$_3$)$_2$O is formed on both surfaces; however, its appearance temperatures are very different, indicating different operative mechanisms. On the powdered surface, it comes from coupling of two CH$_3$O(a). On the other hand, it may be due to “Williamson synthesis” on the single crystal at multilayer coverages.

**CONCLUSIONS**

Our experiments on the interaction of CH$_3$I with TiO$_2$ were carried out on powdered and single-crystal surfaces. On the powdered surface, it belongs to the solid–gas interaction for the experimental conditions used. CH$_3$I dissociates on this surface to form CH$_3$O$_2$(g). Its dissociation rate is enhanced by the presence of isolated hydroxyl groups. In the thermal chemistry, CH$_4$(g) is the major product in the absence of O$_2$. However, only oxygen-containing intermediates and products of CH$_3$O$_2$(g), (CH$_3$)$_2$O(g), CO(g), CO$_2$(g), and H$_2$O(g) are produced in the presence of O$_2$. In the photochemistry, O$_2$ is crucial for CH$_3$I oxidation. On the TiO$_2$ single crystal, the TPD experiment was performed with a multilayer of CH$_3$I. It makes a link to the solid–liquid interaction (41). In the TPD study, (CH$_3$)$_2$O is also found to be the desorption product. (CH$_3$)$_2$O is formed on both surfaces; however, its appearance temperatures are very different, indicating different operative mechanisms. On the powdered surface, it comes from coupling of two CH$_3$O(a). On the other hand, it may be due to “Williamson synthesis” on the single crystal at multilayer coverages.

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