

Crotonaldehyde Formation from Decomposition of $\text{ICH}_2\text{CH}_2\text{OH}$ on Powdered TiO_2

Wen-Chun Wu, Shang-Ju Yang, Chia-Hsun Ho, Yi-Shiue Lin, Li-Fen Liao, and Jong-Liang Lin*

Department of Chemistry, National Cheng Kung University, 1, Ta Hsueh Road, Tainan, Taiwan 701, Republic of China

Received: January 24, 2006; In Final Form: March 9, 2006

Adsorption and reactions of 2-iodoethanol on TiO_2 have been studied by Fourier transform infrared spectroscopy. $\text{ICH}_2\text{CH}_2\text{OH}$ possesses two reactive centers of C–I and C–OH. It is found that its decomposition leads to the formation of crotonaldehyde on TiO_2 . A reaction sequence of $\text{ICH}_2\text{CH}_2\text{OH} \rightarrow \text{ICH}_2\text{CH}_2\text{O}- \rightarrow \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CH}=\text{CH}-\text{CHO}$ is proposed. Although the decomposition routes of $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{I}$, both forming $\text{C}_2\text{H}_5\text{O}-$ on TiO_2 , suggest that $-\text{OCH}_2\text{CH}_2\text{O}-$ may play a role in the crotonaldehyde formation, reaction of $\text{HOCH}_2\text{CH}_2\text{OH}$ on TiO_2 shows that this is not the case. Adsorbed H_2O is formed in the $\text{ICH}_2\text{CH}_2\text{OH}$ decomposition on TiO_2 ; however, it is found that $\text{ICH}=\text{CH}_2$, possibly generated by $\text{ICH}_2\text{CH}_2\text{OH}$ dehydration, is not important in the crotonaldehyde formation.

Introduction

The interaction between alkyl halides and metal (or oxide-supported metal) surfaces has been extensively studied in catalysis, because alkyl halides are useful precursors to generate adsorbed alkyl groups. Our previous study has shown that ethyl iodide molecules dissociate on TiO_2 below 200 °C, forming ethoxide groups due to C–I bond scission and chemical attachment of the ethyls to TiO_2 surface oxygen atoms.¹ Studies of adsorption and reactions of alcohols on TiO_2 are of interest in understanding the surface bonding and reaction steps in the TiO_2 formation by chemical vapor deposition using titanium alkoxides as precursors and in hydrocarbon oxidation. It has been shown that, on TiO_2 , ethanol decomposes to form surface ethoxide groups at 35 °C, but the evolution of gaseous products occurs at a temperature higher than 200 °C.^{1–3} Organic functional groups are generally the reactive centers; however, studies of adsorption and reactions of molecules with multiple functional groups on metal and metal oxide surfaces are scarce. In this research, the $\text{ICH}_2\text{CH}_2\text{OH}$ molecule studied possesses two reactive centers of $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{I}$. Compared to the cases of $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{I}$, there are several intriguing points in the reactions of $\text{ICH}_2\text{CH}_2\text{OH}$ on TiO_2 , including dissociation kinetics of the COH and CI groups and types of surface intermediates and products generated. Besides, TiO_2 is a widely used photocatalyst. It is essential to study the adsorption and thermal decomposition of $\text{ICH}_2\text{CH}_2\text{OH}$ prior to photochemical reactions. It is found that $\text{ICH}_2\text{CH}_2\text{OH}$ decomposes on TiO_2 to form crotonaldehyde ($\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$), which can also be generated by condensation of two acetaldehyde molecules on TiO_2 . However, no crotonaldehyde is generated from $\text{HOCH}_2\text{CH}_2\text{OH}$ or $\text{ICH}=\text{CH}_2$ decomposition on TiO_2 . Because of the limitation in the time-scale of FTIR spectroscopy used in this study, no reaction kinetics is investigated.

Experimental Section

The sample preparation of TiO_2 powder supported on a tungsten fine mesh ($\sim 6 \text{ cm}^2$) has been described previously.^{4,5} In brief, TiO_2 powder (Degussa P25, $\sim 50 \text{ m}^2/\text{g}$, anatase 70%,

rutile 30%) was dispersed in a 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 an IR cell with two CaF_2 windows for IR transmission down to 1000 cm^{-1} . The TiO_2 sample in the cell was heated to 450 °C under vacuum for 24 h by resistive heating. The temperature of the TiO_2 sample was measured by a K-type thermocouple spot-welded on the tungsten mesh. Before each run of the experiment, the TiO_2 sample was heated to 450 °C in a vacuum for 2 h. After the heating, 10 Torr of 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. $\text{ICH}_2\text{CH}_2\text{OH}$ (99%, Aldrich), $\text{ICH}=\text{CH}_2$ (90%, Oakwood), $\text{CH}_3\text{CH}=\text{CH}-\text{CHO}$ (99%, Merck), CH_3CHO (99%, Merck), and $\text{HOCH}_2\text{CH}_2\text{OH}$ (99.97%, Tedia) were purified by several cycles of freeze–pump–thaw prior to introduction into the cell. Infrared spectra were obtained with a 4-cm^{-1} resolution by a Bruker FTIR spectrometer with a MCT detector. The spectra presented here have been ratioed against a clean TiO_2 spectrum providing the metal-oxide background.

Results and Discussion

Adsorption of $\text{ICH}_2\text{CH}_2\text{OH}$ on TiO_2 . Figure 1 shows the infrared spectra of a TiO_2 surface exposed to the saturated vapor of $\text{ICH}_2\text{CH}_2\text{OH}$ at 35 °C, followed by evacuation at this temperature, 50, 100, 150, 200, and 250 °C for 1 min. In the 35 °C spectrum, the infrared peaks appear at 1019, 1066, 1102, 1168, 1185, 1264, 1361, 1382, 1416, 1426, 1456, 1620, 2861, 2925, 2962, and 3018 cm^{-1} . These bands are listed in Table 1 and compared to those of $\text{ICH}_2\text{CH}_2\text{OH}$ observed in the liquid state⁶ and in argon.⁷ It has been reported that $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{O}-$ are coadsorbed on TiO_2 after a TiO_2 surface is exposed to $\text{C}_2\text{H}_5\text{OH}$ vapor at 35 °C.^{1,2} However, $\text{C}_2\text{H}_5\text{I}$ remains intact on TiO_2 at this temperature.¹ In Figure 1, the broad feature at 1620 cm^{-1} indicates the formation of adsorbed H_2O , which is detected in the dissociative adsorption of $\text{C}_2\text{H}_5\text{OH}$ on TiO_2 as well,² showing the evidence of $-\text{COH}$ dissociation of $\text{ICH}_2\text{CH}_2\text{OH}$ on TiO_2 at 35 °C. In terms of the observation of H_2O formation and the previous studies of $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{I}$ on TiO_2 , it is expected that the surface intermediate $\text{ICH}_2\text{CH}_2\text{O}-$ is generated from decomposition of $\text{ICH}_2\text{CH}_2\text{OH}$ on TiO_2 at

* Corresponding author. E-mail: jonglin@mail.ncku.edu.tw.

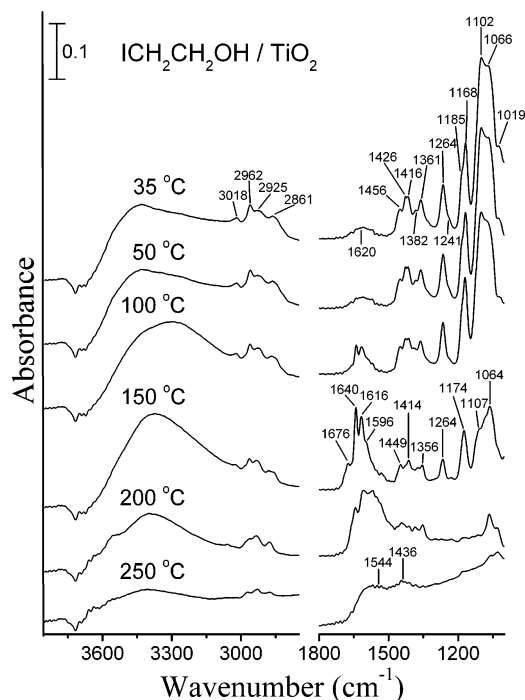


Figure 1. Infrared spectra of a TiO_2 surface taken after being in contact with the saturated vapor of $\text{ICH}_2\text{CH}_2\text{OH}$ at 35 °C, followed by evacuation at this temperature to remove gaseous molecules and then heating at 50, 100, 150, 200, and 250 °C for 1 min in a vacuum. All of the spectra were measured at 35 °C with 50 scans.

TABLE 1: Comparison of Infrared Frequencies (cm^{-1}) of $\text{ICH}_2\text{CH}_2\text{OH}$ in the Liquid State, in Argon, and on TiO_2

liquid ^a	in argon ^b	on TiO_2 , 35 °C (this work)	mode ^{c,d}
3532	3590		$\nu(\text{OH})$
3360			
	3022	3018	$\nu(\text{CH}_2)$
2958	2969	2962	$\nu(\text{CH}_2)$
2930	2939	2925	$\nu(\text{CH}_2)$
2866	2888	2861	$\nu(\text{CH}_2)$
1463			
1457	1459	1456	$\delta(\text{CH}_2)$
1426		1426	
1415	1418	1416	$\delta(\text{CH}_2)$
	1388	1382	$\omega(\text{CH}_2)$
1373	1374	1361	$\delta(\text{COH})$, $\text{tw}(\text{CH}_2)$
	1352		$\omega(\text{CH}_2)$
1265		1264	
1241	1236	1241	$\text{tw}(\text{CH}_2)$
1182		1185	
1169	1150	1168	$\text{tw}(\text{CH}_2)$
1074	1072	1102	$\nu(\text{CO})$, $\nu(\text{C}-\text{C})$, $\delta(\text{COH})$
1033		1066	
1014		1019	

^a Ref 6. ^b Ref 7. ^c Ref 8. ^d ν : stretching; δ : deformation; ω : wagging; tw : twisting.

35 °C and is coadsorbed with $\text{ICH}_2\text{CH}_2\text{OH}$ molecules. Because of the integrity of the $\text{ICH}_2\text{CH}_2\text{O}$ moiety, $\text{ICH}_2\text{CH}_2\text{O}-$ should have infrared bands similar to those of $\text{ICH}_2\text{CH}_2\text{OH}$, as shown in Table 1. In the 35 °C spectrum, the negative bands between 3600 and 3800 cm^{-1} show the decrease of isolated surface OH groups upon $\text{ICH}_2\text{CH}_2\text{OH}$ adsorption on the surface. The broad, enhanced absorptions between 3100 and 3600 cm^{-1} indicate the formation of a hydrogen-bonding system. After heating the surface to 100 °C, two new peaks appear at 1616 and 1640 cm^{-1} . These two peaks continue to grow at 150 °C, accompanied by two shoulders at 1596 and 1676 cm^{-1} . Meanwhile, the peaks belonging to $\text{ICH}_2\text{CH}_2\text{OH}$ and/or $\text{ICH}_2\text{CH}_2\text{O}-$ decrease in intensity significantly. Besides these changes, the hydrogen-bonding absorptions between 3100 and 3600 cm^{-1} are largely

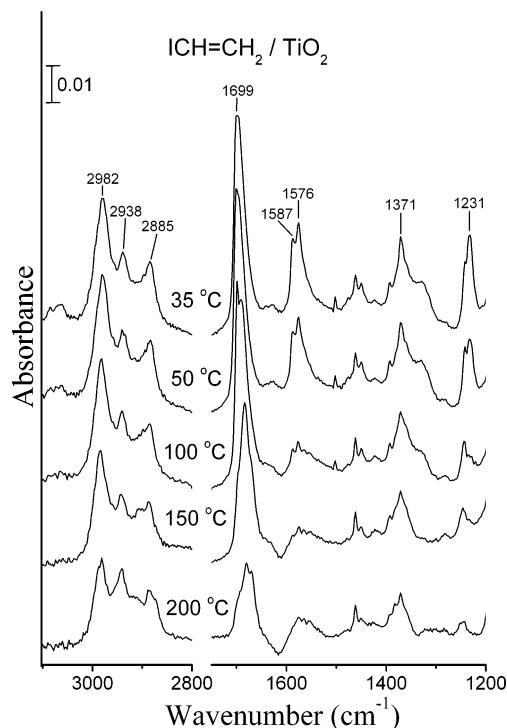


Figure 2. Infrared spectra of a TiO_2 surface taken after being in contact with 2 Torr $\text{ICH}=\text{CH}_2$ at 35 °C, followed by evacuation at this temperature to remove gaseous molecules and then heating at 50, 100, 150, and 200 °C for 1 min in a vacuum. All of the spectra were measured at 35 °C with 50 scans.

increased. This result indicates the increase of associated surface OH groups, possibly generated from C–H dissociation of $\text{ICH}_2\text{CH}_2\text{OH}$ and/or $\text{ICH}_2\text{CH}_2\text{O}-$ on TiO_2 . Because the surface temperature was raised in a vacuum, the appearance of the new peaks and the diminished intensities of $\text{ICH}_2\text{CH}_2\text{OH}$ and/or $\text{ICH}_2\text{CH}_2\text{O}-$ signify a chemical transformation of surface species, instead of readsorption of gaseous reaction products. The peaks from 1596 to 1676 cm^{-1} can be attributed to stretching vibrations of C=C and/or C=O groups.

Adsorption of $\text{ICH}=\text{CH}_2$ on TiO_2 . Figure 2 shows the infrared spectra of a TiO_2 surface exposed to 2 Torr $\text{ICH}=\text{CH}_2$ at 35 °C, followed by evacuation at this temperature, 50, 100, 150 °C. The purpose of this experiment is to demonstrate that $\text{ICH}=\text{CH}_2$ is not generated in the decomposition of $\text{ICH}_2\text{CH}_2\text{OH}$ on the TiO_2 , although the H_2O band (1620 cm^{-1}) observed in the 35 and 50 °C spectra of Figure 1 may suggest the reaction $\text{ICH}_2\text{CH}_2\text{OH} \rightarrow \text{ICH}=\text{CH}_2 + \text{H}_2\text{O}$, and the 1616 and 1640 cm^{-1} bands observed in the 100 and 150 °C spectra indicate that the responsible species may possess C=C functional groups. In the 35 °C spectrum of Figure 2, the main infrared bands appear at 1231, 1371, 1576, 1699, 2885, 2938, and 2982 cm^{-1} . The 1231, 1371, 1576, and 1587 cm^{-1} bands correspond well with those of $\text{ICH}=\text{CH}_2$ reported previously and are attributed to the C–H bending, CH_2 bending, and C=C stretching vibrations of adsorbed $\text{ICH}=\text{CH}_2$, respectively.^{9–11} The 1587 cm^{-1} band is close to the C=C stretching frequency of $\text{ICH}=\text{CH}_2$ in argon; however, the 1576 cm^{-1} band is red-shifted by $\sim 24 \text{ cm}^{-1}$. The latter case is probably due to the interaction of C=C with surface OH or Ti^{4+} . In the 35 °C spectrum of Figure 1, no peaks at 1231 and 1576 cm^{-1} are observed for $\text{ICH}=\text{CH}_2$. In addition, the characteristic $\text{ICH}=\text{CH}_2$ bands at 1231 and 1576 cm^{-1} disappear after heating the surface to 200 °C in a vacuum, without generating 1616 and 1640 cm^{-1} strong bands. This result also reveals that $\text{ICH}=\text{CH}_2$ is not stable on TiO_2 at 150 °C and is not the species responsible for the 1616 and 1640 cm^{-1} bands.

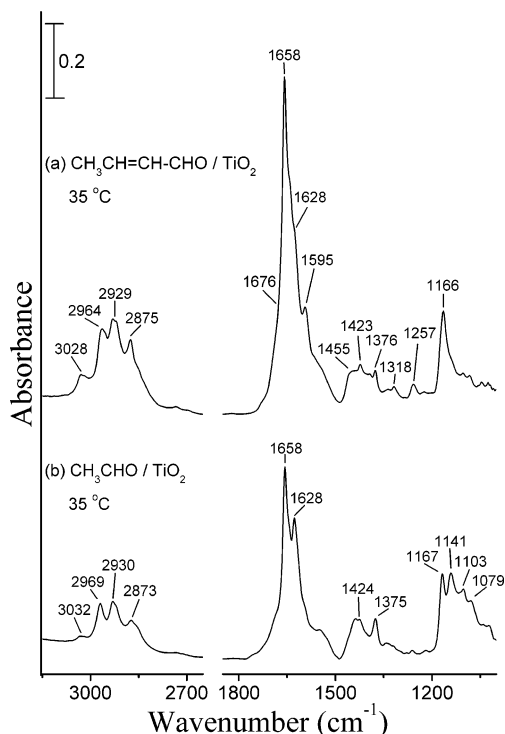


Figure 3. (a) Infrared spectrum of a TiO_2 surface exposed to 2 Torr crotonaldehyde, followed by evacuation at 35 °C; (b) Infrared spectrum of a TiO_2 surface exposed to 2 Torr acetaldehyde, followed by evacuation at 35 °C. All of the spectra were taken at 35 °C with 50 scans.

In Figure 2, the presence of peaks other than those belonging to $\text{ICH}=\text{CH}_2$ shows the decomposition of $\text{ICH}=\text{CH}_2$ on TiO_2 . For example, the 1699 cm^{-1} band suggests the formation of carbonyl groups. Further studies are needed for product identification.

Adsorption of $\text{CH}_3\text{CHCHCHO}$ and CH_3CHO on TiO_2

Figure 3a shows the infrared spectrum of a TiO_2 surface exposed to 2 Torr crotonaldehyde, followed by evacuation at 35 °C. Adsorption of stable crotonaldehyde molecules on anatase and rutile TiO_2 surfaces at 40 °C has been reported.¹² On anatase TiO_2 , infrared bands of crotonaldehyde are located at 1105, 1165, 1394, 1425, 1577, 1636, 1686, 2745, 2845, 2920, 2954, 2979, and 3038 cm^{-1} , similar to the bands of 1098, 1151, 1401, 1425, 1559, 1605, 1664, 2831, 2907, 2952, and 3036 cm^{-1} observed on rutile TiO_2 .¹² In both cases, the $\text{C}=\text{O}$ stretching band (1686 and 1664 cm^{-1} for anatase and rutile, respectively) has the strongest intensity, with the $\text{C}=\text{C}$ one (1636 cm^{-1} for anatase and 1605 cm^{-1} for rutile) as a shoulder. Note that the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ stretching modes of the adsorbed crotonaldehyde are significantly perturbed. The $\text{C}=\text{C}$ and $\text{C}=\text{O}$ stretching frequencies of gaseous crotonaldehyde are 1649 and 1720 cm^{-1} , respectively.¹²

In Figure 3a, the infrared bands appear at 1166, 1257, 1318, 1376, 1423, 1455, 1595, 1628, 1658, 1676, 2875, 2929, 2964, and 3028 cm^{-1} . The bands between 1000 and 1700 cm^{-1} are very similar to those of crotonaldehyde on Degussa-P25 TiO_2 loaded with 2 or 5 wt % Cu in terms of the band positions and their relative intensities.¹³ Crotonaldehyde on TiO_2 can also be generated by acetaldehyde adsorption. Figure 3b shows the infrared spectrum of a TiO_2 surface exposed to 2 Torr acetaldehyde, followed by evacuation at 35 °C. Clearly, the bands at 1167, 1375, 1424, 1628, and 1658 cm^{-1} signify the appearance of crotonaldehyde. Note that, on anatase and rutile TiO_2 surfaces, the infrared bands of adsorbed acetaldehyde

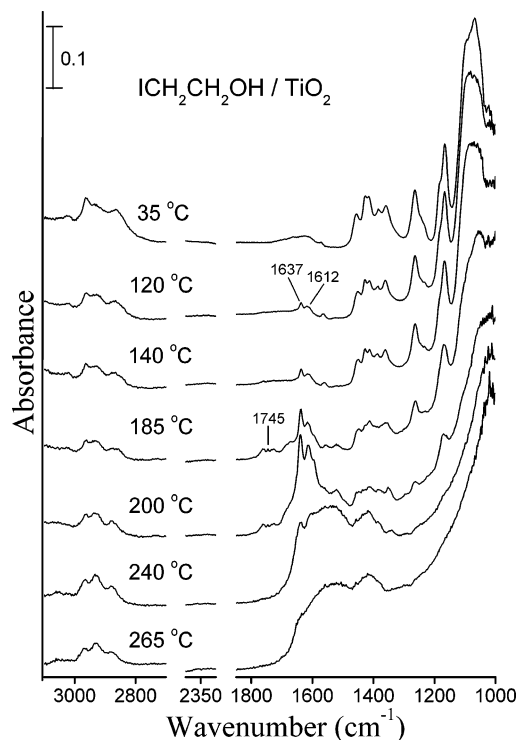


Figure 4. Infrared spectra taken in the heating course of TiO_2 initially in the saturated vapor of $\text{ICH}_2\text{CH}_2\text{OH}$ in a closed cell at 35 °C. The heating rate was 2 °C/s . The spectra were taken at the temperatures indicated with 5 scans.

appear at ~ 1355 and $\sim 1720\text{ cm}^{-1}$.¹² In the 150 °C spectrum of Figure 1, the absorption feature from 1596 to 1676 cm^{-1} well matches that of crotonaldehyde generated by direct crotonaldehyde adsorption or by condensation of two acetaldehyde molecules on TiO_2 , as shown in Figure 3, parts a and b. In addition to the similarity of these $\text{C}=\text{C}$ and $\text{C}=\text{O}$ peaks, the relatively intense 1174 cm^{-1} peak in the 150 °C spectrum of Figure 1 also strongly supports the formation of crotonaldehyde from $\text{ICH}_2\text{CH}_2\text{OH}$ decomposition on TiO_2 . Another strong peak in this spectrum is the 1064 cm^{-1} band which is more intense than the 1107 cm^{-1} peak of $\text{ICH}_2\text{CH}_2\text{OH}$ and/or $\text{ICH}_2\text{CH}_2\text{O}-$, suggesting formation of other products different from crotonaldehyde. As the surface is further increased to 200 °C , the amount of crotonaldehyde decreases largely, as evidenced by the smaller 1640 cm^{-1} peak in Figure 1. In the 250 °C spectrum, two broad absorptions at 1436 and 1544 cm^{-1} are detected. It has been reported that crotonate ($\text{CH}_3\text{CH}=\text{CH}-\text{COO}-$), which is generated from crotonaldehyde decomposition on Cu/TiO_2 , has two broad peaks at 1422 and 1518 cm^{-1} .¹³ In Figure 3a, the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ stretching frequencies appear at 1595 , 1628 , 1658 , and 1676 cm^{-1} . According to the previous study of crotonaldehyde on anatase and rutile TiO_2 ,¹² the 1595 and 1628 cm^{-1} bands can be assigned to the $\text{C}=\text{C}$ modes of crotonaldehyde on rutile and anatase TiO_2 surfaces, respectively, and the 1658 and 1676 cm^{-1} to $\text{C}=\text{O}$ modes of crotonaldehyde on rutile and anatase TiO_2 surfaces, respectively. In the case of crotonaldehyde generated from $\text{ICH}_2\text{CH}_2\text{OH}$ decomposition (150 °C spectrum, Figure 1), the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ stretching modes appear at 1596 , 1616 , 1640 , and 1676 cm^{-1} . On the basis of the infrared frequencies and relative peak intensities, the 1596 and 1616 cm^{-1} are assigned to the $\text{C}=\text{C}$ stretching modes and 1640 and 1676 cm^{-1} to $\text{C}=\text{O}$ stretching ones. Compared to those of gaseous crotonaldehyde, the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ frequencies of the adsorbed crotonaldehyde are significantly red-shifted. This may be due to the interaction of these functional groups with surface

TABLE 2: Comparison of the Infrared Bands (cm⁻¹) of Cyclic Ethylenedioxy (–OCH₂CH₂O–)

K ₂ [OCH ₂ CH ₂ O] ^a	–OCH ₂ CH ₂ O–/Mo(100) ^b	–OCH ₂ CH ₂ O–/O/Ag(100) ^c	–OCH ₂ CH ₂ O–/O/Cu(100) ^d	HOCH ₂ CH ₂ OH TiO ₂ , 100 °C (this work)	mode ^e
858					
883		890 m	880 m		
	1031			1041	$\rho(\text{CH}_2)$
1093		1090 s	1090 s	1089	$\nu(\text{C–O})$
				1118	tw(CH ₂)
				1220	tw(CH ₂) + $\nu(\text{C–C})$
1290					$\omega(\text{CH}_2)$
1370		1340 w		1354	$\omega(\text{CH}_2)$
1445	1455	1450 w		1446	$\delta(\text{CH}_2)$
2833	2857	2860 m		2859	$\nu(\text{CH}_2)$
2899			2880 m	2892	
	2913			2927	$\nu(\text{CH}_2)$

^a Ref 16. ^b Ref 17. ^c Ref 15. ^d Ref 18. ^e w: weak; m: medium; s: strong; ν : stretching; δ : deformation; ω : wagging; tw: twisting; ρ : rocking.

OH or Ti⁴⁺.¹² Besides, the frequencies may also be affected by coadsorbed species, such as iodine which is generated from ICH₂CH₂OH decomposition.

Reaction of ICH₂CH₂OH on TiO₂. Figure 4 shows the infrared spectra taken in the heating course of TiO₂ initially in the saturated vapor of ICH₂CH₂OH in a closed cell. Adsorbed crotonaldehyde is detected at 120 °C, as revealed by the appearance of 1612 and 1637 cm⁻¹ peaks. Gaseous acetaldehyde is also generated, with the representative peak located at 1745 cm⁻¹.¹⁴ This acetaldehyde peak starts to appear between 120 and 140 °C. The detection of acetaldehyde in the gas phase is determined by its amount in the infrared cell, the length of the cell, and the acetaldehyde infrared absorption coefficient.

The acetaldehyde from ICH₂CH₂OH decomposition may recombine to generate crotonaldehyde immediately after formation on the surface and/or readsorb and react on the surface after desorption. Taken together with the result of Figure 3b showing the crotonaldehyde formation of acetaldehyde condensation at 35 °C, it strongly suggests that the ICH₂CH₂OH decomposition on TiO₂ to form crotonaldehyde is via acetaldehyde.

Adsorption of HOCH₂CH₂OH on TiO₂. To further elucidate the crotonaldehyde formation mechanism, adsorption of HOCH₂CH₂OH on TiO₂ was investigated. Figure 5 shows the infrared spectrum for a TiO₂ surface exposed to the saturated vapor of HOCH₂CH₂OH at 35 °C, followed by evacuation at this temperature, 50, 100, and 150 °C for 1 min. Adsorption of HOCH₂CH₂OH on TiO₂ at 35 °C yields absorption bands at 1054, 1086, 1135, 1220, 1354, 1377, 1449, 1620, 2854, 2887, and 2930 cm⁻¹. Dissociative adsorption of simple alcohol molecules, such as methanol and ethanol, on TiO₂ are found to generate the corresponding alkoxy species on the surface.^{1–3} In Figure 5, the appearance of an adsorbed water band at 1620 cm⁻¹ reveals COH dissociation, which is further supported by the strong bands at 1054, 1086, and 1135 cm⁻¹ due to C–O stretching vibrations. The C–O stretching frequencies of liquid HOCH₂CH₂OH molecules appear at 1038 and 1087 cm⁻¹.¹⁵ Both methoxy and ethoxy on TiO₂ have a strong absorption at ~1125 cm⁻¹.² The presence of the 1135 cm⁻¹ band indicates dissociation of COH groups of HOCH₂CH₂OH. After heating the surface to 100 °C, the infrared absorptions at 1089 and 2859 cm⁻¹ are largely enhanced. These two bands remain approximately the same at 150 °C, in contrast to the reduced 1620 cm⁻¹ band due to water desorption. Surface cyclic ethylenedioxy from ethylene glycol decomposition has been isolated on oxygen-covered Ag(110) (O/Ag(110)) and Cu(100) (O/Cu(100)), with the two strongest bands at 1090 and 2860 cm⁻¹ for the former surface and at 1090 and 2880 cm⁻¹ for the latter one. It is not surprising to observe the same species on TiO₂.

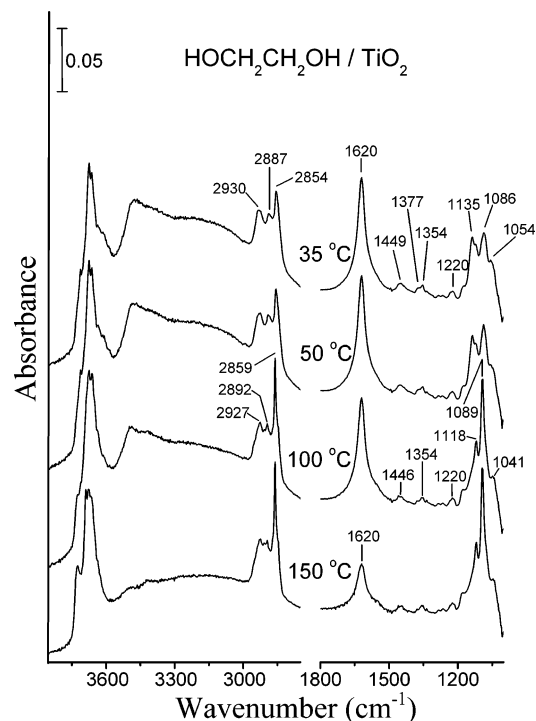
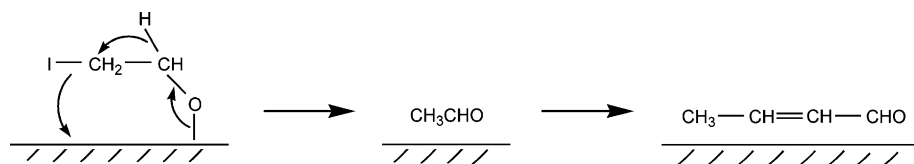


Figure 5. Infrared spectra of a TiO₂ surface taken after being in contact with the saturated vapor of HOCH₂CH₂OH at 35 °C, followed by evacuation at this temperature to remove gaseous molecules and then heating at 50, 100, and 150 °C for 1 min in a vacuum. All of the spectra were measured at 35 °C with 50 scans.

Table 2 compares the infrared bands observed in the 100 °C spectrum to those of K₂[OCH₂CH₂O], –OCH₂CH₂O–/Mo(100), –OCH₂CH₂O–/O/Ag(110), and –OCH₂CH₂O–/O/Cu(100). The 1064 cm⁻¹ peak observed in the 150 and 200 °C spectra of Figure 1 is likely due to –OCH₂CH₂O– species. Most importantly, no crotonaldehyde is generated from HOCH₂CH₂OH decomposition on TiO₂.

Scheme 1 shows a possible ICH₂CH₂OH reaction sequence for the crotonaldehyde formation on TiO₂. On TiO₂, C₂H₅OH decomposes at 35 °C to form C₂H₅O–, in contrast to C₂H₅I dissociation (> 100 °C), also forming C₂H₅O–.^{1,2} Therefore, it is suggested that crotonaldehyde is generated from decomposition of ICH₂CH₂O–. Although –OCH₂CH₂O– can be generated from ICH₂CH₂OH decomposition by bond breakage of C–I and O–H, the HOCH₂CH₂OH adsorption study of Figure 5 shows that –OCH₂CH₂O– cannot produce crotonaldehyde on TiO₂. Because acetaldehyde molecules readily condense to produce crotonaldehyde on TiO₂ at 35 °C (Figure 3b) and is detected in the ICH₂CH₂OH reaction over TiO₂ (Figure 4), it is

SCHEME 1



proposed that crotonaldehyde is generated as $\text{ICH}_2\text{CH}_2\text{O}-$ decomposes to form acetaldehyde as an intermediate. Condensation of two acetaldehyde molecules, forming crotonaldehyde, also leads to the enhanced absorptions between 3100 and 3600 cm^{-1} due to the increase of hydrogen-bonded surface OH groups, as shown in the 100 and 150 $^\circ\text{C}$ spectra of Figure 1. This study of $\text{ICH}_2\text{CH}_2\text{OH}$ on TiO_2 shows an interesting result forming crotonaldehyde, not through $-\text{OCH}_2\text{CH}_2\text{O}-$ as suggested by the individual $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{I}$ decomposition chemistry. In the present study, it is difficult to address the thermal stability of adsorbed iodine by FTIR, since the vibrational frequency of $\text{I}_{(\text{a})}$ is far below our detection limit of 1000 cm^{-1} . But the study of CH_3I decomposition on the TiO_2 -(100) surface has shown that $\text{I}_{(\text{a})}$ is stable up to ~ 300 $^\circ\text{C}$, as evidenced by X-ray photoelectron spectroscopy.¹⁹

Summary

$\text{ICH}_2\text{CH}_2\text{OH}$ decomposes on TiO_2 to form crotonaldehyde. This product is proposed to result from condensation of two acetaldehyde, accompanied by the increase of hydrogen-bonded surface hydroxy groups. On the basis of the bond dissociation temperature of C-I in $\text{C}_2\text{H}_5\text{I}$ and O-H in $\text{C}_2\text{H}_5\text{OH}$, acetaldehyde is proposed to be generated from $\text{ICH}_2\text{CH}_2\text{O}-$ reaction. In addition, dissociative adsorption of $\text{HOCH}_2\text{CH}_2\text{OH}$ does not produce crotonaldehyde that excludes the role of $-\text{OCH}_2\text{CH}_2\text{O}-$ in the crotonaldehyde formation.

Acknowledgment. This research was supported by the National Science Council of the Republic of China (NSC 94-2113-M-006-001).

References and Notes

- (1) Wu, W.-C.; Liao, L.-F.; Shiu, J.-S.; Lin, J.-L. *Phys. Chem. Chem. Phys.* **2000**, 2, 4441.
- (2) Wu, W.-C.; Chuang, C.-C.; Lin, J.-L. *J. Phys. Chem.* **2000**, 104, 8719.
- (3) Hussein, G. A. M.; Sheppard, N.; Zaki, M. I.; Fahim, R. B. *J. Chem. Soc., Faraday Trans.* **1991**, 87, 2661.
- (4) Basu, P.; Ballinger, T. H.; Yates, J. T., Jr. *Rev. Sci. Instrum.* **1988**, 59, 1321.
- (5) Wong, J. C. S.; Linsebigler, A.; Lu, G.; Fan, J.; Yates, J. T., Jr. *J. Phys. Chem.* **1995**, 99, 335.
- (6) Wyn-Jones, E.; Orville-Thomas, W. J. *J. Mol. Struct.* **1967**, 1, 79.
- (7) Homanen, L. *Spectrochim. Acta* **1983**, 39A, 77.
- (8) Thomassen, H.; Samdal, S.; Hedberg, K. *J. Phys. Chem.* **1993**, 97, 4004.
- (9) Torkington, P.; Thompson, H. W. *J. Chem. Soc.* **1994**, Part I, 303.
- (10) Abrash, S. A.; Pimentel, G. C. *J. Phys. Chem.* **1989**, 93, 5834.
- (11) Paolucci, D. M.; Gunkelman, K.; McMahon, M. T.; McHugh, J.; Abrash, S. A. *J. Phys. Chem.* **1995**, 99, 10506.
- (12) Rekoske, J. E.; Barteau, M. A. *Langmuir* **1999**, 15, 2061.
- (13) Coloma, F.; Baeza-Bachiller, B.; Rochester, C. H.; Anderson, J. A. *Phys. Chem. Chem. Phys.* **2001**, 3, 4817.
- (14) *The Aldrich Library of FT-IR Spectra*, 1st ed.; Aldrich: Milwaukee, 1985.
- (15) Capote, A. J.; Madix, R. J. *J. Am. Chem. Soc.* **1989**, 111, 3570.
- (16) Gattow, V. G.; Berg, J. Z. *Anorg. Allg. Chem.* **1974**, 407, 262.
- (17) Queeney, K. T.; Arumainayagam, C. R.; Weldon, M. K.; Friend, C. M.; Blumberg, M. Q. *J. Am. Chem. Soc.* **1996**, 118, 3896.
- (18) Brydon, T. R.; Garrett, S. J. *J. Phys. Chem. B* **2001**, 105, 9280.
- (19) Su, C.; Yeh, J.-C.; Chen, C.-C.; Lin, J.-C.; Lin, J.-L. *J. Catal.* **2000**, 194, 45.