Photo-Catalytic Oxidation of Acetone on a TiO₂ Powder: an *in situ* FTIR Investigation

János Szanyi* Ja Hun Kwak[#]

Institute for Integrated Catalysis, Pacific Northwest National Laboratory

Richland, WA 99354, USA

[#]Current address: Department of Chemical Engineering, UNIST, 100 Banyeon-Ri,
Ulsan 689-798, Korea

*corresponding author: janos.szanyi@pnnl.gov

In situ transmission infrared spectroscopy was used to investigate the photo-oxidation of acetone on a commercial, oxidized TiO₂ (P25) powder catalyst under UV irradiation at ambient temperature, in the absence and presence of gas phase O₂. The photochemistry of a number of organic molecules (2-butanone, methanol and acetic acid,) under the same conditions was also studied in order to identify reaction intermediates and products formed in the photo-oxidation of acetone. Under anaerobic conditions (in the absence of gas phase oxygen) limited extent of photo-oxidation of acetone took place on the oxidized TiO₂ sample. In the presence of O₂ in the gas phase, however, acetone was completely converted to acetates and formates, and ultimately CO₂. The initial step in the sequence of photo-induced reactions is the ejection of a methyl radical, resulting in the formation of surface acetates (from the acetyl group) and formates (from the methyl radicals). Acetate ions are also converted to formates, that, in turn, photo-oxidized to CO₂. Under the experimental conditions applied the accumulation of carbonates and bicarbonates were observed on the TiO₂ surface as the photo-oxidation of acetone proceeded (this was also observed during the course of photo-oxidation of all the other organics studied here). When the initial radical ejection step produced hydrocarbons containing more than one C atoms (as in the case in 2-butanone and mesityl oxide), the formation of aldehydes on the catalyst surface was also observed as a result of secondary reactions.

Keywords: TiO₂; photo-oxidation of acetone; intermediates; reaction mechanism; FTIR spectroscopy.

Introduction:

Since the first reports on the photocatalytic activity of TiO₂ some 40 years ago [1] a tremendous amount of work has been dedicated to the understanding of processes taking place both in the photocatalyst itself, and on the surfaces of these materials. Photo-oxidation of organic compounds (“pollutants”) has been one of the main research directions in the utilization of TiO₂ photocatalysts [2-4]. Studies on a number of TiO₂ polymorphs and a large variety of organic compounds have been conducted. Due to the large variations in the photocatalytic materials

themselves, the reactants studied, reaction conditions applied and UV light used, different conclusions have been reached on the mechanisms of these processes. Systematic studies on model, single crystal TiO_2 samples have greatly enhanced the basic understanding of the processes occurring during UV light initiated surface reactions [5,6]. The photo-oxidation of acetone has been one of the most widely studied photo-catalytic process due to its direct relevance to practical applications and also as a suitable probe molecule for fundamental studies. These studies were conducted on both high surface area powder catalysts and TiO_2 single crystals. El-Maazawi et al. [7] carried out a detailed study on the photo-oxidation of acetone focusing primarily on the effects of acetone coverage and humidity on the rate of photo-oxidation. They identified (by transmission FTIR spectroscopy) a number of species formed on the catalyst surface during acetone exposure and in subsequent UV irradiation. They concluded that three different mechanisms can contribute to the overall photo-catalytic oxidation reaction, and their relative contributions were dependent on the reaction conditions (acetone coverage and humidity). In a recent work Mattson et al. [8] compared the photo-oxidation activities of three different TiO_2 polymorphs: anatase, brookite and rutile. Although they found significant differences in the photo-oxidation paths of acetone, surface formate ions were identified as the key intermediates over all three TiO_2 polymorphs. They also found that strongly bonded surface species (μ -acetate and μ -formate) impeded the decomposition reaction, while too weakly adsorbed species compete with water for surface sites. The most fundamental work on the photo-oxidation of acetone on TiO_2 published in a series of papers by Henderson [9-14]. He investigated the individual steps of the overall process, and concluded that the photo-decomposition of acetone is preceded by a thermal process involving acetone and an adsorbed oxygen species. The photodecomposition of this complex generates a methyl radical (which then can propagate the reaction via radical mechanism) and a surface-bound acetate ion. The rate of further photo-oxidation of the thus formed acetate ion was observed to be at least 2 orders of magnitude slower than the slowest step in acetone photo-oxidation.

Here we report on a study over a commercial TiO_2 (P25) powder photo-catalyst, focused on identifying surface intermediates formed during the photodecomposition/photo-oxidation of adsorbed acetone under UV irradiation, at room temperature, using *in situ* transmission FTIR spectroscopy. These studies were aided by investigations of the photo-oxidation of other organic

molecules (methanol, 2-butanone, acetic acid). We find that under conditions where the in-dark adsorbed surface species is solely acetone, the surface species initially formed is mostly acetate, that subsequently (slowly) converts to formate, and then to CO₂. Formate ions also seem to form directly from the oxidation of the initially ejected methyl radicals. At higher initial acetone coverages mesityl oxide can form prior to UV illumination, and its photo-oxidation path also result in the formation of aldehydes. Similarly, in the photo-oxidation of 2-butanone the formation of adsorbed acetaldehyde was observed as well. The formation of aldehydes seem to be linked to secondary reaction (oxidation) of hydrocarbon radicals formed in the first step if photodecomposition. The final oxidation product, gas phase CO₂ can re-adsorb on the TiO₂ surface forming stable carbonate and bicarbonate species.

Experimental: The TiO₂ sample studied here was a P25 material obtained from Degussa (~70% anatase and ~30% rutile; 50 m²/g surface area). The powder sample was pressed onto a tungsten grid that allowed the transmission of ~80% of the IR beam. A type C thermocouple was spotwelded onto the top center of the W grid that allowed the monitoring of the sample temperature during pretreatment, photo-oxidation and post-reaction TPD. The thus prepared sample was then attached to a sample holder assembly made of copper, and mounted onto a stainless steel tube. All the measurements reported here were carried out in an IR cell constructed from a 2 3/4" stainless steel cube, equipped with CaF₂ windows, connected to both a gas handling manifold and a pumping station, and modified to allow the introduction of UV light through a fiber optics cable. The sample was positioned in the IR cell in a way that allowed both the illumination of the sample with UV light, and the simultaneous collection of IR spectra from the sample (the angle between the plane of the sample and the direction of the IR beam was 45°, while the UV light arrived normal to the sample surface). Prior to each photo-oxidation experiment the sample was calcined in O₂ at 773 K for 2 h, and cooled to room temperature (~300 K) in oxygen. Then the cell was evacuated, a background spectrum was collected, and then the sample was exposed to the organic compound of interest. After equilibration between the organic compound and the TiO₂ sample (i.e., until no more change in the IR spectrum of adsorbed species were seen) the cell was evacuated to remove both the non-reacted and weakly adsorbed organic compound from the cell. The sample was then exposed to UV light even in the absence or in the presence of gas phase O₂, and changes in the adsorbed surface species were

followed by transmission FTIR. Each spectrum reported was the average of 256 scans collected at 4 cm^{-1} resolution. After the completion of each photo-oxidation experiment the cell was evacuated and a TPD (at 12 K/min heating rate, from 300 to 773 K) was run to monitor the species desorbing from the sample. The UV source was a 500 W Hg-Xe lamp (Oriel Corp.), and the UV light was transferred to the sample via a fused silica fiber optic cable. The UV intensity at the sample was kept constant at $\sim 200\text{ mW/cm}^2$ during photo-catalytic measurements. A water filter was used between the UV lamp and the fiber optics cable to minimize heating of the sample by IR radiation. The maximum temperature increase as a result of UV irradiation less than 10 K .

Results and Discussion: In order to unravel the reaction sequence of acetone photo-oxidation on a commercial TiO_2 catalyst (P25), we systematically investigated the surface species present during adsorption and subsequent UV illumination for a series of molecules with transmission FTIR spectroscopy. The identification of most of the IR bands observed during the photo-oxidation of acetone was aided by the investigation of a series of molecules that possess similar functional groups or produce similar surface species during their photo-oxidation reactions. To this end we studied the interactions of methanol, acetic acid, 2-butanone and CO_2 with the TiO_2 surface at room temperature, both in the presence and in the absence of UV irradiation. The results of these studies allow us to unambiguously assign most of the IR features observed during the photo-oxidation of acetone, thus provide information about the sequence of reactions that lead to the mineralization of acetone (oxidation to CO_2) during the photo-oxidation reaction. In the following paragraphs we are going to discuss the interactions of these molecules with TiO_2 , and identify the common surface species (intermediates) formed during adsorption and under UV illumination in the presence of O_2 .

1. Acetone: A. UV irradiation in the absence of gas phase O_2 : First we investigated photoreactions taking place on the acetone-exposed, oxidized TiO_2 surface during UV irradiation in the absence of gas phase oxygen. After exposing the clean, oxidized TiO_2 sample to acetone (less than saturation coverage) the IR spectrum (black line in Fig. 1, collected after 10 min of acetone introduction to the IR cell) displayed features characteristic of adsorbed acetone: ν_{CO} ($1698\text{--}1701\text{ cm}^{-1}$), $\delta_{\text{as}}(\text{CH}_3)$ (1422 cm^{-1}), $\delta_{\text{s}}(\text{CH}_3)$ (1367 cm^{-1}) and $\nu(\text{C-C})$ (1244 cm^{-1}). The

Figure 1. Series of IR spectra collected during the UV irradiation of adsorbed acetone on TiO₂ under anaerobic conditions. (T=302 K) (1st (black) spectrum at $t_{UV}=0$ min, last (red) spectrum at $t_{UV}=76$ min)

positions of these peaks are practically identical to those observed by El-Maazawi et al. [7] on a similar TiO₂ photo-catalyst. Illumination of the acetone-exposed TiO₂ sample to UV light results in changes in the IR spectra. In particular, the intensity of the C=O stretching vibration of adsorbed acetone at 1701-1698 cm⁻¹ decreases rapidly, and drops to about 30% of its pre-UV exposure value after 76 min. of UV exposure. At the same time there is hardly any change in the intensity of the 1683 cm⁻¹ IR band that represent adsorbed acetone molecules in the vicinity of adsorbed H₂O on the catalyst surface. (The presence of small amount water during/after acetone adsorption may be explained by the reaction of reactive oxygen present on the oxidized TiO₂ and some of the incoming acetone substantiated by the appearances of low intensity IR features characteristic of acetates and formates. Some acetone may also go through aldol condensation to form mesityl oxide and water.) (In a separate experiment we co-adsorbed acetone and water on a clean, oxidized TiO₂ sample in order to substantiate the effect of H₂O on the IR absorption bands of adsorbed acetone. The two IR spectra displayed in Fig. S1 clearly indicate that the most intense IR feature of adsorbed acetone (i.e., ν_{CO} at (1698-1701 cm⁻¹) shifts to lower wavenumbers (to 1693 cm⁻¹) after addition of H₂O onto the acetone-exposed TiO₂, while the lower intensity

bands related to different modes of C-H and C-C vibrations are unaffected by the presence of H₂O on the catalyst surface.) The large decrease in the intensity of the band centered at ~1700 cm⁻¹ is accompanied by the appearance and growth of several new features in the 1300-1600 cm⁻¹ spectral region. These new bands represent adsorbed surface species of the photo-decomposition products of acetone in the absence of oxygen in the gas phase. Specifically, IR features characteristic of the acetate (1556 and 1444 cm⁻¹) and formate (1381 and 1354 cm⁻¹) ions appear [8]. On the oxidized TiO₂ sample adsorbed acetone under UV irradiation and in the absence of gas phase oxygen forms acetate ions first by the ejection of a methyl radical [9]. The formation of surface-bound acetate ions require the presence of adsorbed surface oxygen [9]. Some of the thus formed acetate ions can further react with surface oxygen to form formate ions, a commonly observed intermediate in the oxidation of acetone on TiO₂ [7,8]. Since the experiment discussed here was carried out in the absence of gas phase oxygen, the acetate and the subsequent formate formation reactions only proceed to an extent limited by the availability of adsorbed surface oxygen. After 76 min of irradiation the UV source was shut down and a TPD experiment was carried out to follow the evolution of species remained adsorbed on the surface (results not shown). Selected mass fragments of the post-UV irradiation TPD from the oxidized TiO₂ sample are displayed in Fig. S2. The most intense signals originate from the desorption of molecular acetone, with a weak signal from loosely bound CO₂ and water from the limited UV decomposition of acetone. Both the surface species observed by FTIR and the desorbing decomposition products detected in the post-irradiation TPD experiment are consistent with the sequence of photo-oxidation of acetone on TiO₂. The photo-oxidation mechanism of acetone has been extensively studied both on model catalysts (single crystal rutile TiO₂(110) surfaces [9-14]) and on high surface area TiO₂ catalysts [7,8,15-18]. In a series of studies both the thermal and photochemistry of acetone on TiO₂(110) were investigated by TPD and HREELS [9-14]. From the results of low temperature adsorption experiments a series of adsorbed complexes were proposed to form on the TiO₂(110) surface upon acetone exposure (e.g., η^1 -acetone, mesityl-oxide, η^1 -enolate, η^2 -acetate, η^2 -diolate and poly-acetone). In our study we observe primarily the formation of η^1 -acetone during adsorption, while acetate and formate ions form during UV irradiation of adsorbed acetone. The mechanism of the acetate ion formation is probably the same as it was suggested by Henderson [9], i.e., it is initiated by a

thermal reaction between adsorbed acetone and adsorbed oxygen to produce an acetone-oxygen complex. This complex then photo-decomposes to an acetate ion via methyl radical ejection. Under UHV conditions no further reaction of the CH_3 radical was observed, but was proposed to react with the surface in high surface area photo-catalysts [9], like the one we are discussing here. The additional photo-oxidation of the initially formed acetate ion was found to be very slow on the $\text{TiO}_2(110)$ surface, at least 2 orders of magnitude slower than the formation rate of the acetate ion itself [9]. In our experiment, similarly to previous studies on the photo-oxidation of acetone on high surface area TiO_2 [7,8], however, we observed the facile formation and accumulation of surface formates simultaneously with the appearance of the acetate ions. This species may originate from two main sources: either from the further oxidation of the acetate ions, or from the photo-oxidation of CH_3 radicals ejected during the formation of acetate ions with surface oxygen on the TiO_2 catalyst. It is also noteworthy to mention here that no CO_2 , the complete photo-oxidation product, was observed in this experiment by IR spectroscopy (although we have seen desorption of a trace amount of CO_2 during post photo-oxidation TPD at low temperature). This is due, most probably, to the absence of gas phase oxygen in the reactor system: as soon as the surface-adsorbed oxygen is consumed during the photo-reaction of acetone (i.e., in the formation of acetates and formates) there is no, or very limited amount of additional O_2 available to promote the complete decomposition of the surface species formed in the prior reaction step.

B. UV irradiation in the presence of gas phase O_2 : For this experiment we exposed the sample to an identical amount of acetone as in the previous run at 300 K, let the system equilibrate (no gas phase acetone remained) and then introduced a large amount O_2 into the IR cell ($P_{\text{O}_2}/P_{\text{acetone}} \sim 5000$). During acetone adsorption and the introduction of a large amount O_2 into the IR cell we observed no changes in the IR spectra (see the series of IR spectra in Fig. S3). After illuminating the sample with UV light we observed large changes in the IR features of adsorbed acetone. Selected IR spectra collected during UV irradiation of the acetone-exposed TiO_2

sample in the presence of O₂ are displayed in Fig. 2 (5 hrs total irradiation time). The intensity

Figure 2. Series of IR spectra collected during the photo-oxidation of acetone on TiO₂ in the presence of gas phase O₂ in the 1150-1880 cm⁻¹ (panel a) and in the 2250-3100 cm⁻¹ (panel b) spectral regions. (T=302 K) (Shaded spectrum was obtained after acetone adsorption in the presence of O₂, prior to UV irradiation.)

of the most intense IR feature of adsorbed acetone (ν_{CO} at $\sim 1700 \text{ cm}^{-1}$) decreases rapidly with UV irradiation time, while the IR bands of adsorbed decomposition products (primarily acetates and formates) increase gradually. The intensities of selected IR features as a function of UV exposure time are shown in Fig. 3.

Figure 3. Integrated intensities of selected IR features as a function of UV irradiation time during photo-oxidation of acetone on TiO_2 (Data was obtained from the spectra displayed in Fig. 2a.)

This latter figure clearly show that during the 5 hrs of UV exposure practically all the acetone was photo-oxidized, and converted to acetates and formates. The photo-oxidation of acetone in the presence of O_2 is very fast initially, and after only 10 min of UV irradiation more than 70 % of the acetone initially present on the TiO_2 surface disappeared. The conversion of acetone under UV irradiation in the presence of O_2 in the gas phase is much faster than in the absence of O_2 . In the previous paragraph we have shown that as the availability of surface oxygen diminished in the absence of gas phase O_2 , the disappearance of acetone from the surface slowed down dramatically. In the presence of O_2 , however, the surface oxygen coverage is kept high, therefore much faster initial acetone conversion rate is observed in this case. It is interesting to note, that although the initial acetone disappearance rate is much higher in the presence of O_2 , the rate of acetone disappearance after 2 min UV irradiation is similar regardless the presence or

absence of O₂ in the gas phase. This is due, most probably, to the accumulation of decomposition products on the TiO₂ surface that blocks the adsorption sites for O₂. Indeed, the formation of carboxylates (acetates and formates) is the fastest in the time period in which the acetone disappearance rate is the fastest (first 12 min of UV irradiation). Note also that the CO₂ formation is very fast in this initial UV irradiation time period. The formation of CO₂ requires a series of reactions on the TiO₂ surface, which starts with the formation of acetates and formates from the oxidation of acetone. Although the formation rates of both of these intermediates are fast, their subsequent photo-decomposition is slow. This is well illustrated by the intensity variation of the 1445 cm⁻¹ band, assigned to $\nu_{\text{s(COO)}}$ vibration of adsorbed acetate ions. The intensity of this peak increases very fast at the beginning of UV irradiation, since both the acetone coverage and available surface oxygen concentration are high. The intensity of the 1445 cm⁻¹ peak, i.e., the concentration of adsorbed acetate, reaches its maximum at ~12 min UV irradiation time, and then it drops gradually. At the same time the intensity of the broad IR band at ~1550 cm⁻¹ ($\nu_{\text{as(COO)}}$ of adsorbed acetate+formate ions) slowly increases even after the 1445 cm⁻¹ band reached its maximum, and began to drop. These results clearly show the sequential steps taking place during the photo-oxidation of acetone. First the adsorbed acetone is converted to both formates and acetates, but the only intermediate that can produce CO₂ directly is the formate. Initially all three processes (acetate and formate formation as well as formate decomposition) are fast since acetone coverage is maximum at the beginning of the reaction, and surface sites are available for the adsorption of the intermediates. As the acetone coverage drops fast in the initial 12 min of UV irradiation, the rate of acetate accumulation on the surface decreases, and its coverage reaches a maximum. There are two processes that affect the surface concentration of acetate ions: its formation from the decomposition of acetone (very fast process), and its consumption by a subsequent photo-reaction to produce formate ions (slow process). The increase in the intensity of the IR band at ~1550 cm⁻¹ even after the concentration of acetate ions reached a maximum can be explained by the slow decomposition of formates to CO₂. The concentration of gas phase CO₂ throughout the entire UV irradiation time increases, together with the intensity increase of the 1582 cm⁻¹ IR features. The assignment of this last band is not without ambiguity; it has been proposed to represent hydrogen bonded formates [19], bridged bidentate acetates [16] or the carbonyl stretch of bidentate carbonates [20]. Our data is

consistent with this latter assignment, as the intensity of this peak gradually increases with the increase of CO₂ concentration in the gas phase. (In a separate experiment we conducted CO₂ adsorption on the clean, oxidized TiO₂ sample and observed that the most intense IR feature was the one centered at 1580 cm⁻¹ (data not shown).) The last feature we need to assign is the one that is centered at ~1610 cm⁻¹, and gains most of its intensity after extensive decomposition of acetone, and accumulation of CO₂. In prior studies on acetone photo-oxidation this IR feature was not observed. However, in our case this band becomes one of the dominant features after the disappearance of the 1700 cm⁻¹ IR feature of adsorbed acetone. We assign this feature to a bicarbonate species formed by the interaction of adsorbed CO₂ and H₂O (both are products of the photo-oxidation of acetone). At the beginning of UV irradiation the formed CO₂ adsorbs on the TiO₂ surface to produce bidentate carbonates mostly. However, with increasing amounts of CO₂ and H₂O from the photo-oxidation, the bicarbonate formation dominates over the bidentate carbonates. Some of the intensity of the broad 1244 cm⁻¹ IR feature (the lower wavenumber shoulder) represents the γ_{OH} vibration of this surface-bound bicarbonate species. The formation of bicarbonates is common on metal oxides upon the interaction of CO₂ with surface hydroxyl groups [21-24]. When a fully dehydrated (773 K calcined) γ -Al₂O₃ was exposed to CO₂ at 300 K strong, IR features at 1230, 1475, 1645 and 3610 cm⁻¹ were observed in the IR spectrum and were assigned to bicarbonates [21]. It was also noted that the 3610 cm⁻¹ band (ν_{OH} of the bicarbonate species) was not observed on the hydrated alumina sample (calcined at 473 K) due its H-bonding interaction with the surrounding surface hydroxyls and/or H₂O molecules. Similar IR features were observed on ZrO₂ upon its exposure to CO₂: bands at 1224, 1453, 1610 and 3607 cm⁻¹ [22]. (In our case it is also possible that part of the broad 1444 cm⁻¹ band represents the same vibration ($\nu_{\text{s,CO}}$ of bicarbonates) as the 1475/1438 cm⁻¹ band in γ -Al₂O₃ [21], the 1453 cm⁻¹ peak in ZrO₂ [22], and the 1459 cm⁻¹ peak on Ga₂O₃ [23].) Rodriguez et al. [24] have also investigated the interaction of CO₂ with brookite and rutile TiO₂ samples, and found the formation of carbonates and bicarbonates as well. When they exposed a rutile TiO₂ sample to CO₂ at room temperature they obtained IR features at ~1620, ~1420 and ~1220 cm⁻¹ characteristic of bicarbonates on other oxide surfaces [21, 22]. Our data suggest that these bands should be assigned to bicarbonates rather than carbonates as it was stated in reference 24. IR features of bidentate carbonates (1589, 1315, and 1055 cm⁻¹) and bicarbonates (1434 and 1222

cm⁻¹) were also observed by Su et al. [25] on calcined TiO₂ nanoparticles after CO₂ exposure at room temperature. The proposed sequence of reactions taking place on the TiO₂ surface during acetone adsorption and reaction with O₂ under UV irradiation is summarized in Scheme. 1.

Scheme 1. Scheme of photo-oxidation of acetone (at low initial acetone coverage) over TiO₂. The species shown in the scheme were identified by FTIR spectroscopy. (The species in parenthesis (CH₃C=O and CH₃ radicals) were not observed experimentally in this study.)

In the two series of experiments discussed above we established that for complete acetone photo-oxidation to occur, the presence of gas phase O₂ is required. In order to further substantiate this conclusion we plotted the normalized IR intensity of the ν_{C=O} vibrational mode of adsorbed acetone as a function of UV irradiation (in the first 65 min) in Fig. S4. In the absence of O₂ in the gas phase the amount of acetone converted in the first 65 min of UV irradiation over the oxidized TiO₂ catalyst is about 55 %, while in the presence of O₂ it is higher than 90 %. In fact, in the absence of O₂ we were not able to completely remove acetone from the oxidized TiO₂ sample, while acetone was completely oxidized in the presence of O₂ at the low acetone coverage applied in these measurements.

We have also investigated the photo-oxidation of acetone under identical conditions as discussed above, except we increased the initial amount of acetone by 10 fold (P_{O2}/P_{acetone}~500). It has been shown previously [7,9] that acetone can undergo aldol condensation on the surface of TiO₂ at room temperature even in the absence of UV irradiation, producing mesityl oxide:

In fact, El-Maazawi et al. [7] has found that even at low coverages of acetone (<0.05) aldol condensation took place, and above 0.4 surface coverage the gas phase acetone preferentially

adsorbed on the TiO_2 surface as mesityl oxide. In our experiments discussed above we limited the initial acetone exposure in order to avoid the formation of mesityl oxide. By increasing the amount of acetone introduced onto the TiO_2 surface we anticipated to observe the product of aldol condensation, and the effect of the aldol condensation on the photo-oxidation of acetone. In their study El-Maazawi et al. [7] observed the formation of much larger amount of CO_2 when the photo-oxidation of acetone was carried out on a 0.1 ML acetone-covered TiO_2 in contrast to the 0.01 ML acetone-covered sample. Here we were primarily interested in identifying key surface species that form under the two different initial acetone coverages, under otherwise identical conditions (same catalyst pretreatment, sample temperature, O_2 pressure and UV exposure). A series of selected IR spectra collected after the introduction of acetone onto the clean, oxidized TiO_2 sample at 300 K are displayed in Fig. 4. Collection of the black spectrum

Figure 4. Series of IR spectra recorded during the adsorption of acetone on TiO_2 at 300 K (the amount of acetone introduced onto the catalyst is 10x higher than in the previous experiments).

started at the moment of acetone introduction into the IR cell. The most intense IR feature in this spectrum is the $\nu_{\text{C=O}}$ vibration of adsorbed acetone at 1702 cm^{-1} (same as the one we have seen at the low acetone exposure; black spectrum in Fig. 1). However, the intensity of this feature drops very fast as new IR bands appear and develop during subsequent spectral acquisition. Most prominent is the intensity gain of the peak at 1605 cm^{-1} , which represents the $\nu_{\text{C=C}}$ vibration of

adsorbed mesityl oxide [7]. Other IR bands characteristic of the aldol condensation products mesityl oxide ($\nu_{\text{C=O}}$: 1665 cm^{-1} , $\delta_{\text{as(CH}_3\text{)}}$: 1449 cm^{-1} , $\delta_{\text{s(CH}_3\text{)}}$: 1378 cm^{-1} ; $\nu_{\text{C-H}}$: 2939 and 2872 cm^{-1}) and water (δ_{HOH} : 1629 cm^{-1}) also appear and gain intensity in the 10 min duration of spectrum collection (no change in the IR spectra was observed after 7 min of acetone exposure). After establishing the equilibrium between adsorbed acetone and mesityl oxide on the TiO_2 surface the sample was exposed to O_2 (large excess) and IR spectra were collected as the UV light was turned on (for 5 hrs). A selected series of IR spectra as a function of UV irradiation time is displayed in Fig. 5. During the first 25 min of UV irradiation the (from the bottom black

Figure 5. Series of IR spectra collected during the photo-oxidation of acetone on TiO_2 (the initial amount of acetone in the IR cell during this experiment was 10x of that in prior experiments).

spectrum to the green one (8th)) the most important changes in the IR spectra is the decrease in the intensity of the $\nu_{\text{C=C}}$ vibration of adsorbed mesityl oxide at 1598 cm^{-1} , and the concomitant increase in the intensity of a new IR feature at $1730\text{--}1740\text{ cm}^{-1}$. The position of this IR feature suggests the formation of an adsorbed aldehyde species, most probably acetaldehyde. At the same time there is no change in the intensity of the $\nu_{\text{C=O}}$ band of adsorbed acetone (1698 cm^{-1}) can be seen, suggesting the mesityl oxide is more susceptible to photo-oxidation than acetone. In the first 25 min of UV exposure the development of a broad, intense IR feature centered at $\sim 1550\text{ cm}^{-1}$ can also be observed, indicating the formation of carboxylate species, specifically formates

and acetates. The formation of these latter species is also substantiated by the development of other characteristic IR features of acetate and formate species both in the lower and higher wavenumber spectral region (peak assignments are discussed above). At UV irradiation times longer than 30 min the intensity of the main acetone vibrational feature at 1698 cm^{-1} begins to drop, as those of the formate and acetate features increase substantially. After 50 min UV irradiation the intensity of the IR feature of initially formed aldehyde ($1730\text{-}1740\text{ cm}^{-1}$) starts to drop together with that of acetone (10th spectrum from the bottom). Even after 5 hrs of UV exposure (top red spectrum) there are still unreacted aldehyde and acetone on the surface of the TiO₂ sample. The main surface species formed, however, are acetates and formates. A mechanism for the photo-catalytic oxidation of acetone has been proposed by Xu et al., [17], claiming that the first step was the aldol condensation to form mesityl oxide. This reaction is a thermal process, requiring no UV irradiation. Under UV irradiation and in the presence of oxygen they proposed the formation and the subsequent photodecomposition of formates to the final product CO₂. No discussion on any intermediates that would produce the adsorbed formates was given. In our study we also observe the facile formation of surface formates when the acetone/mesityl oxide mixed layer is exposed to UV. However, we also observe the transient formation of aldehydes (either formaldehyde or acetaldehyde, or both). In fact, during the course of mesityl oxide decomposition we clearly see the accumulation of this latter species, which subsequently consumed in the photo-oxidation process only after all the mesityl oxide was converted. As we mentioned above, the IR data we obtained show that the acetone surface coverage stays high until all the mesityl oxide is consumed. This can be explained by either the different reactivity of acetone in the presence of mesityl oxide (in comparison to acetone in the absence of mesityl oxide), or by the formation of acetone as a result of mesityl oxide decomposition. When acetone adsorbed on TiO₂ in the presence of O₂ is irradiated with UV light, it ejects a methyl radical, and forms a surface acetate ion, while the methyl radical can further react on the TiO₂ surface to form surface formates. In the case of adsorbed mesityl oxide the most probable initial process upon UV illumination is the breaking of the C-C bond that produces $\text{CH}_3\text{-C=O}\cdot$ and $\cdot\text{CH=C(CH}_3)_2$ radicals. These two radicals then react with the TiO₂ surface to form acetate ions, adsorbed formaldehyde, and acetone. This reaction sequence could explain the accumulation of aldehydes and acetates on the surface, and the unchanged coverage

of adsorbed acetone during mesityl oxide decomposition. At the same time, while mesityl oxide decomposition takes place, these newly formed species can further react to form CO_2 (we indeed observed the accumulation of gas phase CO_2 in the IR cell immediately after UV exposure). As mesityl oxide is decomposed, the surface coverages of the aldehyde, acetate, formate and acetone intermediates began to drop. This sequence of reactions seems to be supported by the post irradiation TPD results shown in Fig. 6. After 5 hr UV irradiation the IR cell was evacuated, and

Figure 6. Mass spectrometer signal intensities of selected mass fragments obtained during TPD following the UV photo-oxidation of acetone on TiO_2 .

the sample temperature was increased to 773 K while MS data was collected at every 5 K sample temperature (this series of MS spectra is shown in Fig. S5). The first desorbing species is weakly held CO_2 (44 amu), followed by unreacted acetone (43, 15 amu). Then there is a broad desorption feature of 30 amu which originates from a H_2CO species. This is most probable originating from unreacted aldehyde. The next feature is an intense CO feature (28 amu) representing the decomposition of surface formates, followed by the decomposition at ~650 K of the most stable surface species, acetates (this species decomposes as CH_2CO (42 amu) (ketene)). The decomposition of most of these species was accompanied by the formation of H_2O .

2. Photo-oxidation of 2-Butanone, Methanol and Acetic Acid: In order to support the identification of surface intermediates in the photo-oxidation of acetone, we also investigated the photo-oxidation of 2-butanone, methanol and acetic acid. These experiments were carried out under identical conditions discussed for acetone: room temperature adsorption of the organic compound followed by O₂ exposure and then UV irradiation. The photo-oxidation of 2-butanone has been studied by Henderson [26] on a model photo-catalyst, TiO₂(110). It was determined that, similarly to the photo-oxidation of acetone, the first step in the process was the formation of a diolate species on the TiO₂ surface, which was followed by the ejection of an ethyl radical from this surface species. The product of this process was adsorbed acetate, identical to that seen in the photo-oxidation of acetone. Therefore, we expect to see the formation of very similar surface species in the photo-oxidation of 2-butanone to that we have observed in the acetone photo-oxidation. The main difference we might expect to see can come from the secondary reactions of the ethyl radical with the catalyst surface. (In the UHV study of Henderson [26] the only secondary reaction observed was the dehydrogenation of the ethyl radical to form ethane, but no stable surface species were observed.)

A series of IR spectra obtained during the photo-oxidation of adsorbed 2-butanone are displayed in Fig. 7. The spectra obtained are very similar to those discussed above for the photo-oxidation

Figure 7. Series of IR spectra recorded during the photo-oxidation of 2-butanone on TiO₂ at 310 K.

of acetone (at low acetone coverage in Fig. 2) in the presence of O₂. The primary difference between these two data sets is the development of an absorption feature at 1740 cm⁻¹ during 2-butanone photo-oxidation. We attribute this band to the $\nu_{C=O}$ vibration of adsorbed, H-bonded acetaldehyde [27] originating from the reaction of the initially ejected ethyl radical with surface oxygen [26]. Although the IR spectrum of adsorbed 2-butanone is somewhat different from that of adsorbed acetone (mainly due to the presence of an ethyl group in place of a methyl group in acetone), the IR bands resulting from the photo-oxidation of 2-butanone are identical to those we have discussed for acetone. This observation clearly demonstrate that the photo-decomposition path of 2-butanone is similar to that of acetone: first the ethyl radical is ejected from the adsorbed 2-butanone molecule forming an adsorbed acetyl group, that in turn converts to an acetate by interacting with a surface oxygen. From this point on the reaction proceed the same way as it has been discussed for acetone. The main difference is the formation of acetaldehyde, and its subsequent slow photo-oxidation. The position of the $\nu_{C=O}$ vibrational feature (1740 cm⁻¹) suggests that this species is H-bonded to the surface through the O atom. The intensity of this feature stays constant in the last three spectra, underlining the slow photo-oxidation of this species. (Since there is still a small amount of 2-butanone present on the surface even after 5 hrs of UV irradiation acetaldehyde is constantly being replenished.)

The photo-oxidation of methanol on the same TiO₂ sample was investigated under reaction conditions identical to those discussed above. After the adsorption of methanol O₂ was introduced into the IR cell in large excess and the sample was irradiated with UV light while IR spectra were collected. The series of selected IR spectra recorded during the 5 hrs of UV

irradiation are displayed in Fig. 8. The IR bands observed after $\text{CH}_3\text{OH}+\text{O}_2$ introduction (prior

Figure 8. Series of IR spectra obtained during the photo-oxidation of methanol on TiO_2 at 310 K.

to UV irradiation) correspond to both adsorbed methanol and methoxy groups. Some of the methanol undergoes dissociative adsorption on the oxidized TiO_2 catalyst, and the resulting

CH₃O bind to surface Ti⁴⁺ ions. (Molecular methanol exhibits $\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{sym}}(\text{CH}_3)$ vibrations at 2954 and 2849 cm⁻¹, respectively. These vibrational modes of adsorbed methoxy groups are seen at 2930 and 2815 cm⁻¹, in agreement with prior studies on methanol/TiO₂ systems [28-30].) The IR spectrum (bright green) after 1 min of UV irradiation shows dramatic changes: very large drops in the intensities of both molecularly and dissociatively adsorbed methanol, accompanied by the appearances of intense IR features characteristic of surface-bound formate species ($\nu_{\text{C-H}}(\text{HCOO})$ at 2872 cm⁻¹, and $\nu_{\text{C=O}}$ at 1546 cm⁻¹, $\nu_{\text{sym}}(\text{COO})$ at 1360 cm⁻¹, $\delta_{\text{C-H}}$ at 1379 cm⁻¹). The intensities of these latter vibrational bands increase gradually with UV irradiation time, while the IR features of methoxy groups lose intensities, and at the end of UV irradiation (5 hrs) they completely disappear. During the UV irradiation we can also see the accumulation of gas phase CO₂ in the IR cell (2349 cm⁻¹). After the CO₂ partial pressure reaches a certain level carbonates (1586 and 1413 cm⁻¹) and then, at high CO₂ pressures bicarbonates (1608 and 1242 cm⁻¹) begin to form, and these bands dominate the IR spectrum at the end of the experiment. These results, in agreement with prior studies on the photo-oxidation of methanol [27], show that methanol in the presence of gas phase oxygen is readily converted to formate under UV irradiation on TiO₂. In turn, the thus formed formates then decompose to produce CO₂. The first step of this process, i.e., oxidation of methoxy to formate, is very fast under the conditions applied in this work. However, further oxidation of the adsorbed formate to CO₂ is slow. Even when most of the methanol/methoxy disappeared from the catalyst, the intensities of the IR bands representing formate species are still very high. Since we started out the reaction with a C₁ molecule, CH₃OH, the formation of acetates was not possible. This experiment allowed us to clearly identify IR bands representing formates and carbonate/bicarbonate species without the presence of IR bands of adsorbed acetates.

The last organic molecule we have investigated was acetic acid. Throughout our discussions in the previous paragraphs we claimed the formation of surface-bound acetate ions in the photo-oxidation of acetone and 2-butanone, based on IR peak assignments from earlier publications. In order to fully support those assignments on our catalyst and under our experimental conditions, we studied the photo-oxidation of acetic acid under identical conditions we have discussed above for acetone and 2-butanone. The series of selected IR spectra recorded during the UV irradiation of an acetic acid exposed TiO₂ photo-catalyst in the presence of gas phase O₂ is displayed in Fig.

9. The bottom spectra (shaded grey) correspond to acetic acid adsorbed on TiO_2 in the presence

Figure 9. Series of IR spectra recorded during the photo-oxidation of acetic-acid on TiO_2 at 310 K.

of O_2 , but without UV irradiation. The two most intense IR features at 1527 cm^{-1} (with a shoulder at around 1550 cm^{-1}) and 1450 cm^{-1} (with a shoulder at around 1420 cm^{-1}) represent the $\nu_{\text{a, COO}}(\text{CH}_3\text{COO})$ and $\nu_{\text{sym, COO}}(\text{CH}_3\text{COO})$ vibrational modes of adsorbed acetate ions [7,32, 33]. Additional characteristic IR bands of adsorbed acetate ions at 1335 cm^{-1} (δ_{CH_3}), 1027 cm^{-1} (ρ_{CH_3}) and 1048 cm^{-1} ($\nu_{\text{C-C}}$) are also clearly visible. (The $\nu_{\text{C-H}}$ vibrational feature of the CH_3 group was observed at 2936 cm^{-1} (not shown) in agreement with the results of previous studies [33]. As the UV light is turned on the intensities of these acetate-related IR features decrease immediately, and continue to drop throughout the 5 hrs of illumination (note, that even at the end of the UV irradiation there is still appreciable amount of unreacted acetate present on the TiO_2 surface.) The only species we observe in the IR spectra as a result of UV irradiation is adsorbed formate, carbonate and bicarbonate ions. The photo-decomposition of acetate ions has been studied in great detail on model, single crystal TiO_2 surfaces. On a rutile $\text{TiO}_2(011)$ surface

Idriss et al. [31] have observed the formation of C_2H_6 and CO_2 (by mass spectrometer) when the surface was exposed to acetic acid and oxygen. In our study the formation of ethane was not observed, rather the adsorbed acetate ions were converted to formates, which then were further oxidized to CO_2 and H_2O . Under the conditions applied in this study, the conversion of acetate ions to formate ions were faster than the subsequent photo-oxidation of the formate ions (to CO_2), which resulted in the accumulation of the latter on the surface.

Conclusions: In this study we have identified and followed the surface species formed during the photodecomposition and photo-oxidation of acetone on a commercial TiO_2 catalyst surface using *in situ* transmission FTIR spectroscopy. Our IR band assignments were aided by photo-oxidation experiments carried out on a number of organic molecules (2-butanone, methanol and acetic acid) under identical reaction conditions (room temperature, in large excess of molecular oxygen, and constant UV light intensity). The results obtained have confirmed that the initial step in the photo-oxidation of adsorbed acetone is the ejection of a methyl radical to produce adsorbed acetate and formate ions. Formate ions can form by two reaction paths: either from the decomposition of acetate ions (confirmed by the photo-oxidation of acetic acid) or by the reaction of the ejected methyl radical with active oxygen species on the surface of TiO_2 catalyst. This process most probably takes place through a surface methoxy species, however in these experiments we did not observed methoxy accumulation in a detectable amount during acetone photo-oxidation. This process is very fast, as it was evidenced by the very fast conversion of adsorbed methoxy species (from methanol adsorption) to formates. CO_2 produced by the slow decomposition of adsorbed formates react with the TiO_2 surface to produce both carbonate and bicarbonate species. The photo-oxidation of 2-butanone produced the same adsorbed surface species as that of acetone, except in this case we also observed the formation of acetaldehyde, originating from the secondary reaction of the initially ejected ethyl group with active surface oxygen. We also observed the fast formation of adsorbed mesytil oxide from the aldol condensation reaction of adsorbed acetone (this reaction was not seen in the experiments carried out at low acetone coverages). The photo-oxidation of mesytil oxide also yielded adsorbed aldehydes that converted to carboxylates in subsequent oxidation steps.

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Graphical Abstract: