FTIR Study of Adsorption and Surface Reactions of $N(CH_3)_3$ on TiO_2

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Fourier transform infrared spectroscopy has been employed to investigate the $N(CH_3)_3$ adsorption, thermal stability, and photochemical reactions on powdered TiO_2. $N(CH_3)_3$ molecules are adsorbed on TiO_2 without dissociation at 35 °C and are completely desorbed from the surface at 300 °C in a vacuum. The CH_3 rocking frequencies of $N(CH_3)_3$ on TiO_2 are affected via the interaction between $N(CH_3)_3$ and TiO_2 surface OH groups. In the presence of O_2, adsorbed $N(CH_3)_3$ decomposes thermally at 230 °C and photochemically under UV irradiation. In the latter case with comparative $^{16}O_2$ and $^{18}O_2$ studies, $CO_{2(g)}$, $NCO_{(a)}$, $HCOO_{(a)}$, and surface species containing C═N or NH_x functional groups are identified to be the photoreaction products or intermediates. In the presence of $^{18}O_2$, the main formate species formed is $HC^{16}O^{18}O_{(a)}$. As H_2O is added to the photoreaction system, a larger percentage of adsorbed $N(CH_3)_3$ is consumed. However, in the presence of $^{18}O_2$ and H_2O, the amount of $HC^{16}O^{18}O_{(a)}$ becomes relatively small, compared to $HC^{16}O^{16}O_{(a)}$. A mechanism is invoked to explain these results. Furthermore, based on the comparison of isotopic oxygens in the formate products obtained from $CH_3O_{(a)}$ photooxidation in $^{16}O_2$ and $^{18}O_2$, it is concluded that the $N(CH_3)_3$ photooxidation does not generate $CH_3O_{(a)}$ in which the oxygen belongs to TiO_2.

Introduction

Photoreactions of some nitrogen-containing organics catalyzed by semiconductors in solution phase have been investigated. Various reaction types were reported, depending on the molecular structures of reactants.[1−6] For example, under irradiation, aniline and toluidine in ethanol with suspended ZnO and dissolved O_2 were transformed into the corresponding azocompounds;[1] imides were generated from *N*-acylamine reactions in the presence of oxygenated aqueous suspensions of TiO_2;[2] primary amines reacted to form secondary amines in aqueous solution containing a powdered mixture of TiO_2 and platinum black[4,5] and to form *N*-alkylidene amines in the presence of suspended TiO_2 in acetonitrile.[6] The semiconductor-catalyzed photoreactions were surface chemical processes; however, adsorption and surface reactions were not characterized.

TiO_2, a semiconductor with a ∼3.2 eV band gap, has often been used as a photocatalyst in solar energy conversion and degradation of molecules detrimental to the environment. Previously, Primet et al. used $N(CH_3)_3$ as a probe molecule to investigate acidic properties of TiO_2 and suggested that $N(CH_3)_3$ was adsorbed on the Lewis acid sites and some surface OH groups of anatase TiO_2 showed a protonic acidity.[7] Boccuzzi et al. observed the thermal decomposition of adsorbed $N(CH_3)_3$ on TiO_2 at 473 K in O_2 atmosphere.[8] To our knowledge, a more detailed study of interaction between $N(CH_3)_3$ and TiO_2 has not been reported. $N(CH_3)_3$ is moderately toxic by inhalation and is used in organic synthesis, manufacture of disinfectants, etc. In the present study, adsorption, thermal stability, and photoreactions of $N(CH_3)_3$ on powdered TiO_2 are examined by Fourier transform infrared spectroscopy in a gas−solid interaction system.

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Experimental Section

The sample preparation of TiO_2 powder supported on a tungsten fine mesh (∼6 cm^2) has been described previously.[9,10] In brief, TiO_2 powder (Degussa P25, ∼50 m^2/g, anatase 70%, rutile 30%) was dispersed in water/acetone solution to form a uniform mixture that was then sprayed onto a tungsten mesh. After that, the TiO_2 sample was mounted inside the IR cell for simultaneous photochemistry and FTIR spectroscopy. The IR cell with two CaF_2 windows for IR transmission down to 1000 cm^{-1} was connected to a gas manifold that was pumped by a 60 L/s turbomolecular pump with a base pressure of $\sim 1 \times 10^{-7}$ Torr (1 Torr = 1.33×10^{-3} bar). 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 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. The TiO_2 surface after the above treatment still possessed residual isolated hydroxyl groups.[11] $^{16}O_2$ (99.998%, Matheson) and $^{18}O_2$ (99 atom %, Isotec) were used as received in compressed states. $N(CH_3)_3$ (45% aqueous solution, Merck-Schuchardt) was purified by several cycles of freeze−pump−thaw and introduced to the cell as the solution was cooled to ∼3 °C to reduce the solubility of $N(CH_3)_3$ in the water and the evaporation of water molecules. Pressure was monitored with a Baratron capacitance manometer and an ion gauge. In the photochemistry study, both the UV and IR beams were set 45° to the normal of the TiO_2 sample. The UV light source used was a combination of a Hg arc lamp (Oriel Corp), a water filter, and a band-pass filter with a bandwidth of ∼100 nm centered at 400 nm (Oriel 51670). The UV absorption of $N(CH_3)_3$ for the wavelengths used in the present study was negligible.[12] Infrared spectra were obtained with a 4 cm^{-1}

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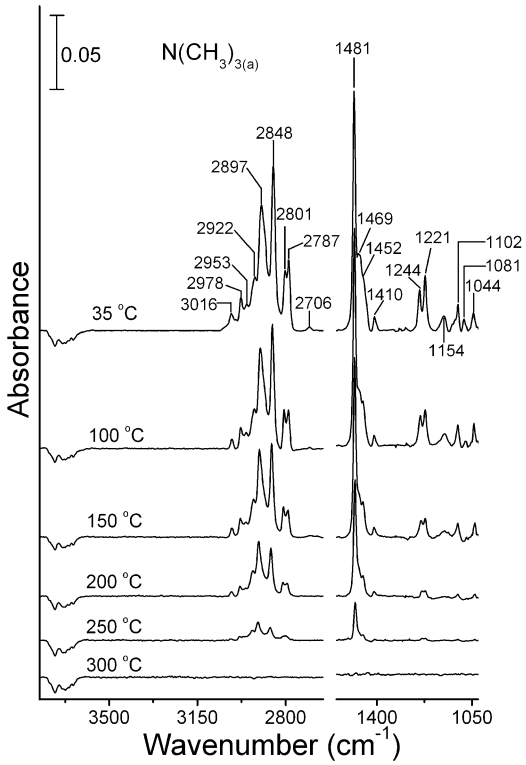


Figure 1. Infrared spectra of a TiO_2 surface exposed to ~0.4 Torr of $N(CH_3)_3$ and then evacuated at the indicated temperatures for 1 min. All the spectra were recorded at 35 °C with 50 scans.

resolution by a Bruker FTIR spectrometer with a MCT detector. The entire optical path was purged with CO_2-free dry air. The spectra presented here have been ratioed against a clean TiO_2 spectrum providing the metal-oxide background. In the study of photooxidation, the photoirradiation time count was started as the UV lamp was turned on. It took 40−50 s to reach full power. It was noted that in the present studies the infrared band frequencies obtained from different runs of experiments with the same conditions might vary by a few wavenumbers.

Results and Discussion

Adsorption of $N(CH_3)_3$ on TiO_2. Figure 1 shows the infrared spectra of a TiO_2 surface after being in contact with ~0.4 Torr of $N(CH_3)_3$ at 35 °C, followed by evacuation at the indicated temperatures for 1 min. All of the spectra in Figure 1 were taken at ~35 °C. Before analyzing the infrared spectra, it is worthy to note the CH_3 decoupling feature of $N(CH_3)_3$.[13−15] In each CH_3 group of $N(CH_3)_3$, the C−H bond, trans to the lone-pair electrons of the N atom, has a lower stretching strength than that of the other two C−H bonds. The decoupling of the CH_3 into CH and CH_2 groups can be reasoned that the internal motion of the methyl group is so slow compared to the IR time scale that each of the C−H bonds is localized in one of the three potential minima. Another $N(CH_3)_3$ infrared absorption feature is that it shows relatively strong overtone and combination bands. In the 35 °C spectrum of Figure 1, infrared bands appear at 1044, 1081, 1102, 1154, 1221, 1244, 1410, 1452, 1469, 1481, 2706, 2787, 2801, 2848, 2897, 2922, 2953, 2978, and 3016 cm^{-1}. Table 1 compares the infrared frequencies of $N(CH_3)_3$ in the gas phase[14] and on Ni(111),[15] Pt(111),[16] and TiO_2 of the present work. Our observed frequencies at 1044 ($\nu_{as}(NC_3)$), 1102 ($\rho'(CH_3)$), 1410 ($\delta_s(CH_3)$), 1469 ($\delta''_{as}(CH_3)$), 2953 ($\nu_s(CH_2)$), and 2978 cm^{-1} ($\nu_{as}(CH_2)$) agree well with the corresponding fundamental modes of gaseous $N(CH_3)_3$, with a discrepancy ≤3 cm^{-1}. This resemblance indicates the presence of $N(CH_3)_3$ on TiO_2. The 2787 cm^{-1} ($\nu_s(CH)$) band of the adsorbed $N(CH_3)_3$ is 11 cm^{-1} higher than that of gaseous $N(CH_3)_3$. For the 1186 and 1275 cm^{-1} CH_3 rocking bands of gaseous $N(CH_3)_3$, no closely matched bands are observed in the 35 °C spectrum of Figure 1, but at 1081, 1154, 1221, and 1244 cm^{-1} instead. This implies either some of the $N(CH_3)_3$ molecules dissociate, forming new surface species responsible for the infrared bands, or the interaction between adsorbed $N(CH_3)_3$ and TiO_2 surface alters some of the infrared frequencies of the surface $N(CH_3)_3$. The TiO_2 surface used in this study possessed isolated OH groups, Ti^{4+} Lewis acid sites, and Ti^{3+} defect sites.[17−19] In the theoretical calculations of NH_3 adsorption on rutile TiO_2, it has been shown that NH_3 can be bound to surface OH via hydrogen bonding and to Ti^{4+} via Lewis acid−base interaction.[20] Similar interactions may apply to the adsorbed $N(CH_3)_3$ on powdered TiO_2. Furthermore, previous studies of hydrogen bonding interactions between hydrogen halides (HF, HCl, HBr, and HI) and $N(CH_3)_3$ showed that the CH_3 rocking modes of $N(CH_3)_3$ in $N(CH_3)_3$−hydrogen halide complexes were indeed significantly affected, compared to those of free $N(CH_3)_3$ molecules.[21−23] For example, the 1269 cm^{-1} rocking band of free $N(CH_3)_3$ is shifted to 1215 cm^{-1} after forming an acid−base complex with HF in Ar matrix; the $N(CH_3)_3$−HCl complex absorbs at 1004, 1197, and 1220 cm^{-1}, in contrast to the 1043, 1186, and 1275 cm^{-1} of free $N(CH_3)_3$ molecules. Similarly, the $N(CH_3)_3$−HBr complex absorbs at 1000, 1196, and 1225 cm^{-1} and the $N(CH_3)_3$−HI complex absorbs at 1002, 1206, and 1250 cm^{-1}. In the 35 °C spectrum of Figure 1, the negative bands in the 3500−3800 cm^{-1} region represent the decrease of isolated OH groups on TiO_2 after $N(CH_3)_3$ adsorption, indicating the presence of interaction between the surface OH groups and adsorbed $N(CH_3)_3$ and corroborating the lower CH_3 rocking frequencies of $N(CH_3)_3$ on TiO_2. Although the interaction between adsorbed $N(CH_3)_3$ and surface OH groups is evidenced, the interaction between adsorbed $N(CH_3)_3$ and Ti^{4+} cannot be ruled out.

From the temperature-dependent spectra shown in Figure 1, the band intensities of adsorbed $N(CH_3)_3$ decrease upon heating to 100 °C and disappear at a temperature of 300 °C in a vacuum, without forming new bands. This result suggests that $N(CH_3)_3$ is molecularly adsorbed on the surface at 35 °C and totally

TABLE 1: Comparison of Infrared Frequencies (cm^{-1}) of $N(CH_3)_3$ in the Gas Phase and on Various Surfaces

gas phase (ref 14)	assignment[a]	Ni(111), 110 K (ref 15)	Pt(111), 85 K (ref 16)	TiO_2, 308 K (this work)
1043	$\nu_{as}(NC_3)$		1041	1044
				1081
1103	$\rho'(CH_3)$		1098	1102
1186	$\rho'(CH_3)$	1205	1187	1154
				1221
1275	$\rho''(CH_3)$		1271	1244
1409	$\delta_s(CH_3)$			1410
1459	$\delta'_{as}(CH_3)$	1463	1455	1452
1466	combination band			
1471	$\delta''_{as}(CH_3)$	1470		1469
1478	combination band			1481
2737	combination band			2706
2776	$\nu_s(CH)$	2763	2731, 2768	2787
2824	overtone	2822		2801
2874	overtone	2873		2848
2898	combination band			2897
2940	combination band			2922
2953	$\nu_s(CH_2)$		2817, 2945	2953
2981	$\nu_{as}(CH_2)$		2973	2978
				3016

[a] ν: stretching. δ: deformation. ρ: rocking.

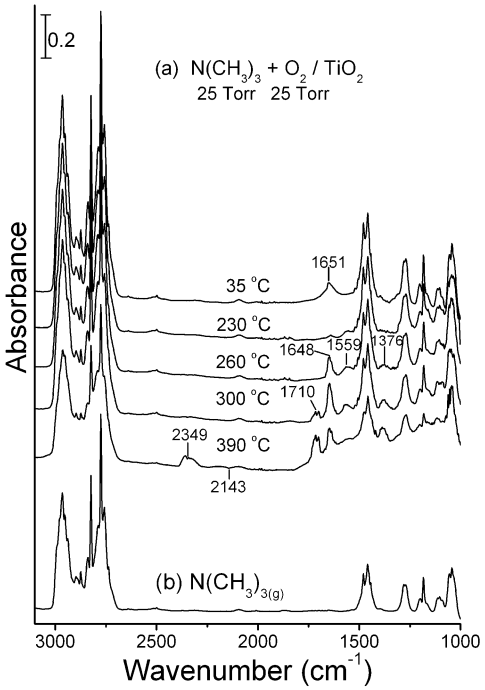


Figure 2. (a) Development of infrared spectra of a mixture of ~25 Torr of $N(CH_3)_3$ and ~25 Torr of O_2 over a TiO_2 surface heated at a rate of 2 °C/s; (b) infrared spectrum of gaseous $N(CH_3)_3$. All the spectra in part a were recorded at the indicated temperatures with 5 scans.

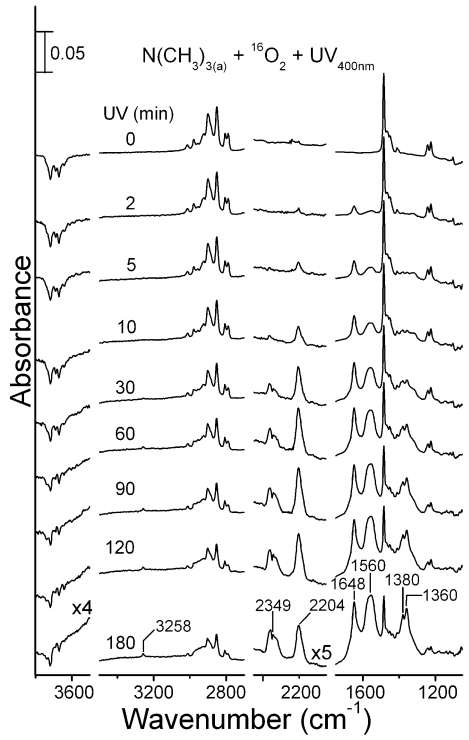


Figure 3. Infrared spectra taken after the indicated times during UV irradiation of $N(CH_3)_3$ adsorbed on TiO_2 initially in 10 Torr of $^{16}O_2$ in a closed cell. All the spectra were recorded with 5 scans. All the traces in 2050−2450 and 3500−3800 cm^{-1} are multiplied by a factor of 5 and 4, respectively.

desorbed without dissociation after heating to 300 °C. There is other indirect evidence that supports the molecular adsorption of $N(CH_3)_3$ on TiO_2. If the C−N bonds of $N(CH_3)_3$ dissociate, adsorbed CH_3O groups are expected to be generated, because the dissociative CH_3I adsorption, via C−I bond scission, on TiO_2 has shown the formation of adsorbed CH_3O.[24] CH_3O on TiO_2 absorbs at ~1045, 1125, 2825, and 2925 cm^{-1}.[25] If the C−H bonds of $N(CH_3)_3$ dissociate, surface OH absorptions between 3500 and 3800 cm^{-1} and/or C═N absorptions between 1580 and 1690 cm^{-1} are expected to be enhanced.[26] But this is not the case in the present study.

Thermal Reactions of $N(CH_3)_3$ on TiO_2 in the Presence of O_2. Figure 2a shows the spectra taken at the indicated temperatures for a mixture of ~25 Torr of $N(CH_3)_3$ and ~25 Torr of O_2 initially in contact with a TiO_2 surface at 35 °C in a close cell. The surface temperature was increased linearly from 35 °C to 400 °C at a rate of 2 °C/s. A gaseous $N(CH_3)_3$ spectrum is also shown in Figure 2b for comparison. The 35 °C spectrum of Figure 2a can be attributed to the absorptions of $N(CH_3)_3$ present on TiO_2 and in the gas phase. However, the broad peak at 1651 cm^{-1} is probably due to the combination mode (1640 cm^{-1}) of $N(CH_3)_3$[14] overlapped with the bending mode of adsorbed H_2O, which is introduced to the cell at such a high $N(CH_3)_3$ dosage. As the temperature is increased to 230 °C, this band becomes smaller because of the partial desorption of adsorbed $N(CH_3)_3$ and H_2O. Six new bands appear at 1376, 1559, 1648, 1710, 2143, and 2349 cm^{-1} during the heating process up to 400 °C. It has been reported that $HCOO_{(a)}$ produced from HCOOH dissociative adsorption on TiO_2 has two strong absorption bands at 1370 and 1555 cm^{-1}.[27] Formamide also dissociates on TiO_2, producing adsorbed η^2(N,O)-HCONH with two strong bands at 1355 and 1568 cm^{-1}.[28] Additionally, in the investigation of the NO_2/TiO_2 adsorption system heated at 375 °C, three bands at 1360, 1440 (relatively small), and 1550 cm^{-1} have been measured. The 1440 and 1550 cm^{-1} bands are suggested to be due to a nitro−nitrito complex, i.e., attached to the Ti^{4+} ion by N and O atoms simultaneously.[29] Therefore, the 1376 and 1559 cm^{-1} bands observed in Figure 2 are likely due to HCOO, HCONH, and/or a nitro−nitrito complex on the surface. The 1648 and 1710 cm^{-1} bands are assigned to C═N and C═O stretching vibrations.[26] The carbonyl stretching modes of formic acid[27] and formamide[28] on TiO_2 have been detected at ~1680 cm^{-1}. Because of not enough evidence, the responsible species for the 1648 and 1710 cm^{-1} bands are not determined. The 2143 and 2349 cm^{-1} bands are due to CO and CO_2 formed in the gas phase, respectively. The 1559 cm^{-1} band appears at 230 °C, revealing that $N(CH_3)_3$ dissociates on TiO_2 at this temperature. A similar thermal experiment was also carried out, but without O_2. It was found that, except for the infrared bands belonging to $N(CH_3)_3$, no new bands were detected.

Oxidation of $N(CH_3)_3$ on TiO_2 under Photoirradiation in the Presence of O_2. Figure 3 shows the infrared spectra taken after the indicated times during 400 nm photoirradiation of a TiO_2 surface covered with $N(CH_3)_3$ initially in 10 Torr of $^{16}O_2$. Inspecting the change of the spectra with photoirradiation time, it is found that the amount of adsorbed $N(CH_3)_3$ decreases and that new bands appear, indicating photodecomposition of $N(CH_3)_3$ and formation of new species. The new bands resulting from $N(CH_3)_3$ photodecomposition appear at 1360, 1380, 1560, 1648, 2204, 2349, and 3258 cm^{-1} after 180 min of photoirradiation. The 1560 and 1648 cm^{-1} bands appear in the early illumination stage, ~2 min. Among the observed new bands, the 2349 cm^{-1} band is directly attributed to gaseous CO_2 and its size increases continuously with photoirradiation. To correctly assign the other observed bands, photooxidation of $N(CH_3)_3$ on TiO_2 in $^{18}O_2$ was investigated as well. Figure 4 shows the infrared spectra taken after the indicated times during 400 nm of photoirradiation of a TiO_2 surface covered with $N(CH_3)_3$ in 10 Torr of $^{18}O_2$. In the infrared analysis for Figures 3 and 4, the band assignments are based on characteristic frequencies

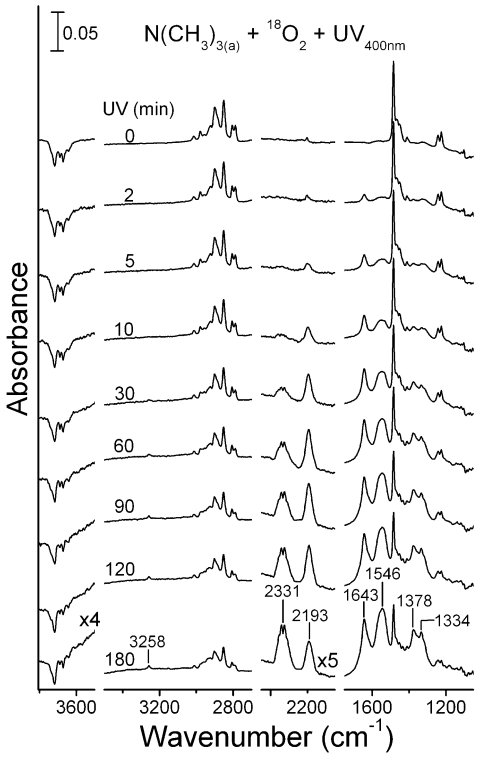


Figure 4. Infrared spectra taken after the indicated times during UV irradiation of $N(CH_3)_3$ adsorbed on TiO_2 initially in 10 Torr of $^{18}O_2$ in a closed cell. All the spectra were recorded with 5 scans. All the traces in 2050−2450 and 3500−3800 cm^{-1} are multiplied by a factor of 5 and 4, respectively.

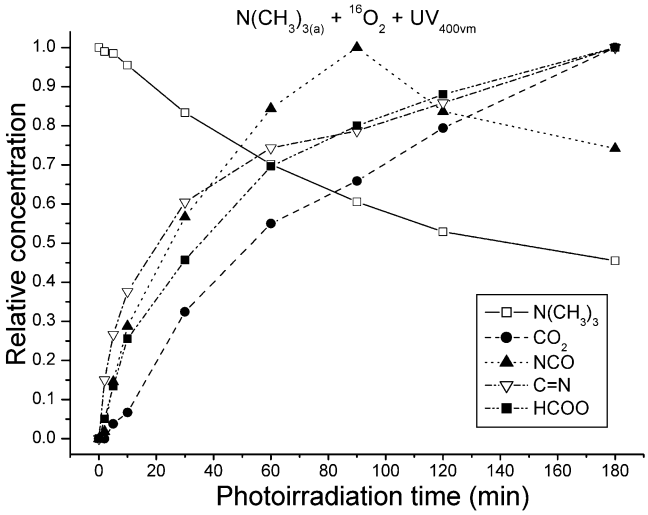


Figure 5. Relative concentrations of the major species detected in the photodecomposition of $N(CH_3)_{3(a)}$ on TiO_2 in $^{16}O_2$ as a function of photoirradiation time. The maximum amount for each species during the irradiation process is scaled to 1.

of functional groups and shifts in frequency of oxygen-containing species.[26,30] Compared to the bands found in the $^{16}O_2$ case, any red-shifted bands in Figure 4 suggest that the species responsible for them possess ^{18}O. As an example, the 2349 cm^{-1} $C^{16}O_{2(g)}$ band in the $^{16}O_2$ case is red-shifted to 2331 cm^{-1} in the 180 min spectrum of Figure 4, which is attributed to $C^{18}O_{2(g)}$. Other red-shifted bands with a frequency difference larger than 10 cm^{-1} include the 1334 cm^{-1} shifted from 1360 cm^{-1}, 1546 cm^{-1} from 1560 cm^{-1}, and 2193 cm^{-1} from 2204 cm^{-1}. The 1378 and 1643 cm^{-1} bands are shifted, to a smaller extent, from 1380 and 1648 cm^{-1}, respectively. The band at 3258 cm^{-1} does not change in frequency and is assigned to the NH_x stretching mode. The 1643 cm^{-1} band belongs to the stretching vibration of the C═O or C═N functional group. However, the former functional group seems unlikely, because C═^{18}O stretching vibrations of organic compounds are expected to be about 25 cm^{-1} lower than C═^{16}O stretching vibrations.[26] The 2204 cm^{-1} band observed in Figure 3 is attributed to isocyanate species, $NCO_{(a)}$. In the recent studies of photooxidation of CH_3CN on TiO_2 in O_2, a similar band has been observed.[31,32] The shift of the band at 2204 cm^{-1} in $^{16}O_2$ to 2193 cm^{-1} in $^{18}O_2$ is consistent with the CN frequency of $NC^{16}O_{(a)}$ being higher than that of $NC^{18}O_{(a)}$ on TiO_2 by a ∼10 cm^{-1}.[32] On TiO_2, $NCO_{(a)}$ formation has been reported first from the decomposition of isocyanic acid at 25 °C.[33] The two strong bands at 1360 and 1560 cm^{-1} observed in the $^{16}O_2$ case are shifted to lower frequencies in the $^{18}O_2$ case by 26 and 14 cm^{-1}, respectively. The 1360 and 1560 cm^{-1} bands are assigned to −COO− symmetric and antisymmetric stretching of $HCOO_{(a)}$, with supports from the previous observation of similar frequencies of $HCOO_{(a)}$ produced by the dissociative adsorption of formic acid and formaldehyde on TiO_2.[27,34,35] In the oxygen isotopic study for HCOONa, the symmetric stretching of $-C^{16}O^{16}O-$, $-C^{16}O^{18}O-$, and $-C^{18}O^{18}O-$ absorb at 1340, 1315, and 1297 cm^{-1}, respectively. On the other hand, the antisymmetric stretching of $-C^{16}O^{16}O-$ and $-C^{18}O^{18}O-$ absorb at 1607 and 1587 cm^{-1}, respectively.[36] The observed frequency shifts in Figures 3 and 4 for symmetric and antisymmetric stretching of formate on TiO_2 are consistent with the case of HCOONa. In addition, the 1380 cm^{-1} band in Figure 3 and the 1378 cm^{-1} band in Figure 4 are assigned to the C−H deformation of formate on TiO_2.[35] This comparative result of $^{16}O_2$ and $^{18}O_2$ also indicates the incorporation of O_2 in the formation of $HCOO_{(a)}$ and $NCO_{(a)}$ from $N(CH_3)_3$ photodecomposition on TiO_2.

Figure 5 shows the relative concentrations of $N(CH_3)_{3(a)}$ and its photodecomposition products of $CO_{2(g)}$, $NCO_{(a)}$, $HCOO_{(a)}$, and the adsorbed species containing the C═N group as a function of photoirradiation time for Figure 3. The $N(CH_3)_3$ decreases continuously with increasing irradiation time in contrast to the monotonically increased $CO_{2(g)}$, $HCOO_{(a)}$, and C═N. $NCO_{(a)}$ increases to a maximum at 90 min and then decreases. In addition, 50% of the OH negative band area that is due to initial $N(CH_3)_3$ adsorption is restored after 180 min of photoirradiation, as shown in Figure 3.

Oxidation of $N(CH_3)_3$ on TiO_2 under Photoirradiation in the Presence of H_2O and O_2. Figure 6 shows the infrared spectra taken after the indicated times during 400 nm of photoirradiation of a TiO_2 surface covered with $N(CH_3)_3$ and $H_2{}^{16}O$ in 10 Torr of $^{16}O_2$. The TiO_2 surface subject to photoirradiation was prepared by adsorption of $N(CH_3)_3$, followed by exposure of H_2O vapor of ∼0.4 Torr and evacuation at 35 °C. In the 0-min spectrum, the infrared band of adsorbed H_2O is located at 1624 cm^{-1}. Similar to the case without H_2O, $HCOO_{(a)}$ (1360, 1381, and 1566 cm^{-1}), $NCO_{(a)}$ (2204 cm^{-1}), $CO_{2(g)}$ (2349 cm^{-1}), and a species containing the C═N group (1645 cm^{-1}) are generated upon photoirradiation. However, there are several different aspects. First, a band at 1173 cm^{-1} appears. Second, $NCO_{(a)}$ increases to a maximum at 60 min and then declines. Third, a larger percentage of adsorbed $N(CH_3)_3$ is consumed in the presence of H_2O, i.e., 85% after 180 min of photoirradiation as compared to the 50% without H_2O in Figure 3. The larger percentage of consumption of $N(CH_3)_3$ in the presence of H_2O and O_2 may result from an increase of reactive initiation species for $N(CH_3)_3$ decomposition, such as O_2^-, hole, or $OH^\bullet$, or acceleration of consumption of the surface intermediates. In the former case, the recent chemiluminescence study has shown that the steady-state O_2^-

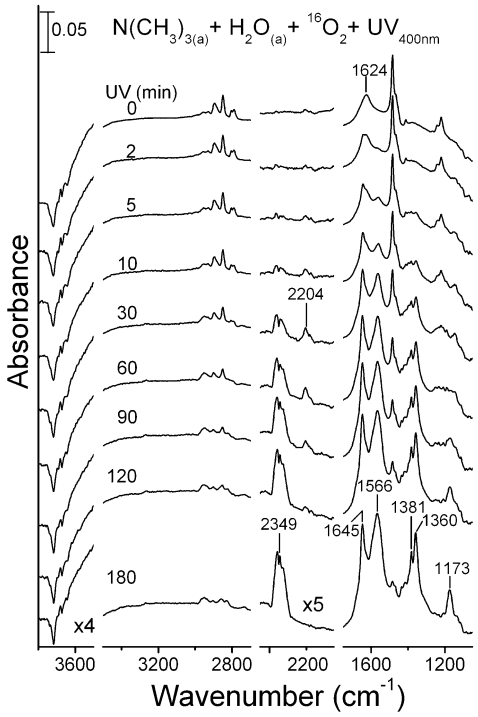


Figure 6. Infrared spectra taken after the indicated times during UV irradiation of a TiO_2 surface covered with $N(CH_3)_3$ and H_2O initially in 10 Torr of $^{16}O_2$ in a closed cell. All the spectra were recorded with 5 scans. All the traces in 2050−2450 and 3500−3800 cm^{-1} are multiplied by a factor of 5 and 4, respectively.

concentration produced for the TiO_2-H_2O−air system under UV illumination is twice that for the TiO_2−air system.[37] O_2^- is a possible initiation species for $N(CH_3)_3$ decomposition. Besides, O_2^- originates from photoelectron capture of O_2, therefore the lifetime of holes can increase because of the retardation of electron−hole pair recombination, inducing more consumption of $N(CH_3)_3$ on TiO_2. Furthermore, it is believed that photoholes can react with surface H_2O to form $OH^•$ radicals. If $OH^•$ is the active species, the presence of H_2O is expected to cause more $N(CH_3)_3$ molecules to decompose. In Figure 6, the 1168 cm^{-1} band falls in the absorption range of the C−N or C−N−C stretching vibration.[26] This peak cannot be assigned to NO, NO_2, or NO_3 species on TiO_2, because the infrared studies of adsorption of NO and NO_2 on TiO_2 have shown no bands at ∼1170 cm^{-1}. NO on TiO_2 absorbs at ∼1900 cm^{-1}.[38] Adsorption of NO_2 on TiO_2 generates surface NO_2 and NO_3 species with infrared absorptions between 1220 and 1640 cm^{-1}.[29] In addition, no band near 1170 cm^{-1} has been observed in the study of photooxidation of NH_3 on TiO_2 in O_2.[39] Photoirradiation of $N(CH_3)_3$ on TiO_2 in the presence of H_2O only, without O_2, was also investigated, but no infrared bands other than those of $N(CH_3)_3$ were observed during the irradiation.

Figure 7 shows the infrared spectra taken after the indicated times during 400 nm of photoirradiation of a TiO_2 surface covered with $N(CH_3)_3$ and $H_2{}^{16}O$ in $^{18}O_2$. In this experiment, it is expected that the same species as those observed in Figure 6 are formed, but H_2O participation in the photoproduct formation is able to be studied. Most interestingly in Figure 7, the formate absorbs at 1356 and 1565 cm^{-1} with a small shoulder at 1332 cm^{-1}. This result indicates that most of the formate molecules generated in the presence of $H_2{}^{16}O$ and $^{18}O_2$ possess two ^{16}O atoms, in contrast to the case in the presence of $^{18}O_2$ only, as shown in Figure 4. H_2O indeed involves in the formation of $HCOO_{(a)}$ in the photodecomposition of $N(CH_3)_3$ on TiO_2.

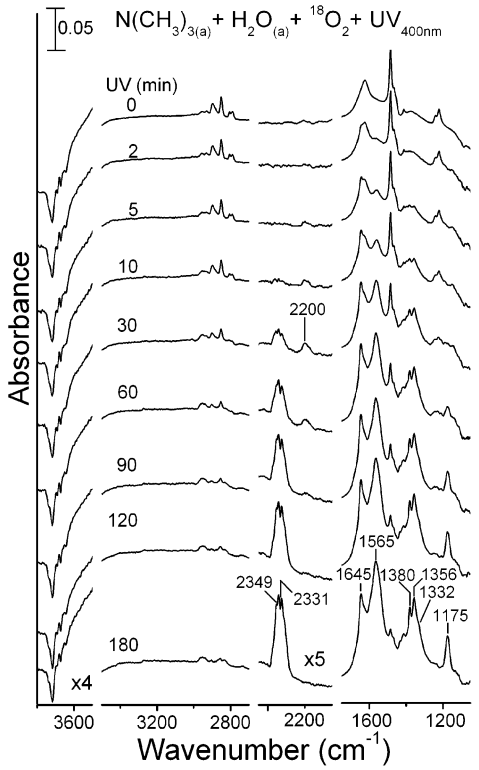


Figure 7. Infrared spectra taken after the indicated times during UV irradiation of a TiO_2 surface covered with $N(CH_3)_3$ and H_2O initially in 10 Torr of $^{18}O_2$ in a closed cell. All the spectra were recorded with 5 scans. All the traces in 2050−2450 and 3500−3800 cm^{-1} are multiplied by a factor of 5 and 4, respectively.

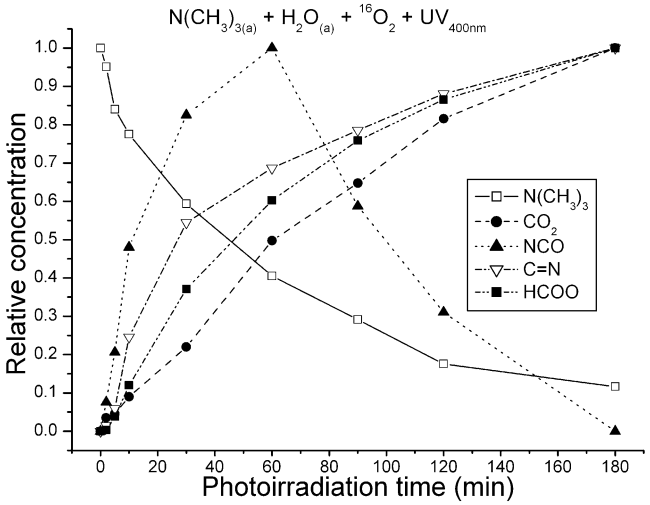
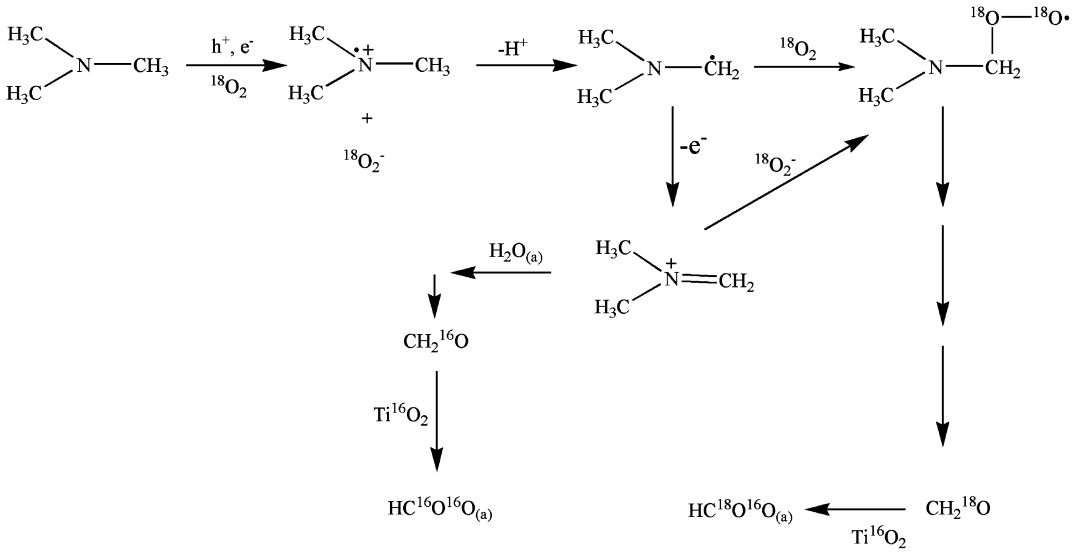


Figure 8. Relative concentrations of the major species detected in the photodecomposition of $N(CH_3)_{3(a)}$ on TiO_2 in the presence of adsorbed H_2O and gaseous $^{16}O_2$ as a function of photoirradiation time. The maximum amount for each species during the irradiation process is scaled to 1.

Figure 8 shows the relative concentrations of $N(CH_3)_{3(a)}$ and its photodecomposition products of $CO_{2(g)}$, $NCO_{(a)}$, $HCOO_{(a)}$, and the adsorbed species containing the C═N group as a function of photoirradiation time for Figure 6. In comparison of Figures 5 and 8, it is found that a larger percentage of adsorbed $N(CH_3)_3$ is consumed after 180 min of photoirradiation in the presence of adsorbed H_2O. As observed in the 0-min spectra of Figures 3 and 6, the areas of the isolated OH negative bands are approximately the same. Using the same preparation process for a clean TiO_2 surface prior to $N(CH_3)_3$ adsorption, which would produce similar surface OH groups, the comparable

SCHEME 1



negative OH band areas suggest that the amounts of isolated surface OH groups on TiO_2 before $N(CH_3)_3$ photodecomposition are comparable for Figures 3 and 6. Therefore the difference in photoreactivity of $N(CH_3)_{3(a)}$ in the presence of $H_2O_{(a)}$ cannot be ascribed to the isolated OH groups. In the present study, the surface temperatures were raised to approximately 43 °C during photoirradiation experiments of $N(CH_3)_3$ on TiO_2. Therefore, thermal control experiments were carried out with the same conditions as those of the photoexperiments, but holding the TiO_2 surface at the corresponding temperatures without photon exposure. No decomposition of $N(CH_3)_3$ in these thermal experiments was observed.

Photooxidation of organic molecules catalyzed by TiO_2 is often suggested to be initiated by holes (or their trapped forms), OH•, and/or anionic oxygens, such as O_2^-. As $N(CH_3)_3$ molecules are attacked by these reactive species, $(CH_3)_2N-CH_2^{\bullet}$ radicals are likely to be formed.[1−6] One of the reaction routes for $(CH_3)_2N-CH_2^{\bullet}$ is its recombination with O_2. This process is the origin for $NCO_{(a)}$ and $HCOO_{(a)}$ formation in the $N(CH_3)_3$ photodecomposition on TiO_2 in O_2. The formation of the intermediate with the C═N functional group can be ascribed to dehydrogenation and N−C bond scission of $N(CH_3)_3$. In fact, it has been reported that two 2-aminobutane $(CH_3(H)C(NH_2)-C_2H_5)$ molecules recombine to form $C_2H_5(CH_3)C{=}NC(H)-(CH_3)C_2H_5$ in anhydrous acetonitrile with suspended TiO_2 powders upon photoirradiation.[6] Although in the present study the N−C bonds break in the $N(CH_3)_3$ photodecomposition mediated by TiO_2, no $CH_3O_{(a)}$ (with infrared absorptions at ∼2825 and 2925 cm^{-1} for CH_3 stretching vibrations and between 1000 and 1200 cm^{-1} for C−O stretching vibrations)[25] formation is observed. However, $CH_3O_{(a)}$ may be a transient species formed in the $N(CH_3)_3$ photooxidation on TiO_2, i.e., it decomposes immediately after it is generated. This point has been clarified by performing a comparative study of $CH_3O_{(a)}$ photooxidation, forming adsorbed formate groups, in $^{16}O_2$ and $^{18}O_2$, as shown in Figure 9. In Figure 9a, $CH_3{}^{16}O_{(a)}$ in $^{16}O_2$ is photooxidized to form $H_2{}^{16}O_{(a)}$ (1625 cm^{-1}) and $HC^{16}O^{16}O_{(a)}$ (1360 and 1560 cm^{-1} for −COO− stretching vibrations). In the presence of $^{18}O_2$ as shown in Figure 9b, new peaks formed at 1335 and 1546 cm^{-1} are attributed to $HC^{16}O^{18}O_{(a)}$, but the main formate species is $HC^{16}O^{16}O_{(a)}$. Compared to the $N(CH_3)_3$ photodecomposition in $^{16}O_2$ and $^{18}O_2$ (Figures 3 and 4), $HC^{16}O^{18}O$ is the dominant form for the latter case. Therefore, it is concluded that, in the photodecomposition of $N(CH_3)_3$ on TiO_2 in O_2, $CH_3O_{(a)}$ is unlikely to be the main reaction intermediate for $HCOO_{(a)}$ formation. Besides, by invoking previously proposed reaction steps of amine oxidation,[3,40−42] the mechanism in Scheme 1 is suggested to explain the observed isotopic form of formate species in the presence of O_2 and/or H_2O. In the photodecomposition of $N(CH_3)_3$ on TiO_2, it must involve multiple bond-forming and bond-breaking steps, i.e., the photodecomposition proceeds via multiple elementary reactions in order to form oxygenated compounds such as $HCOO_{(a)}$, $NCO_{(a)}$, etc. There are very likely other reaction intermediates not detected in the present study. Further studies are necessary for understanding a more complete $N(CH_3)_3$ photodecomposition process. It is interesting to make a com-

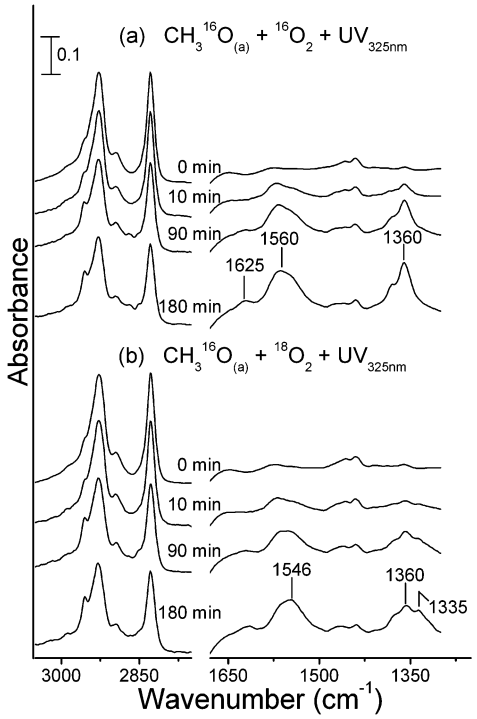


Figure 9. Infrared spectra taken after the indicated times during UV irradiation of a TiO_2 surface covered with CH_3O in 10 Torr of $^{16}O_2$ (a) and $^{18}O_2$ (b). The adsorbed CH_3O was prepared by CH_3OH adsorption on TiO_2 at 35 °C, followed by brief annealing to ∼250 °C in a vacuum.

parison between the previous study of $N(C_2H_5)_3$ on TiO_2 and present study of $N(CH_3)_3$.[43] Because of the shifted CH_3 rocking frequencies of $N(CH_3)_3$ on TiO_2, the interaction between the surface OH and adsorbed $N(CH_3)_3$ is clearly manifested. $N(CH_3)_3$ and $N(C_2H_5)_3$ thermally decompose on TiO_2 at a temperature higher than 200 °C in the presence of O_2. Photooxidation of both $N(CH_3)_3$ and $N(C_2H_5)_3$ on TiO_2 in O_2 generates $NCO_{(a)}$, $HCOO_{(a)}$, and $CO_{2(g)}$. $H_2O_{(a)}$ and $CH_3COO_{(a)}$ are also observed as photoproducts in the case of $N(C_2H_5)_3$. As suggested in the present study, $CH_3COO_{(a)}$ may not be derived from direct C−N bond scission of $N(C_2H5)_3$. The present $N(CH_3)_3$ study also shows that the effect of H_2O addition in the photoreaction of $N(CH_3)_3$ in O_2 is not due to surface OH groups.

Conclusions

On TiO_2, $N(CH_3)_3$ molecules can be bound to surface OH groups and Lewis acid Ti^{4+} ions. The adsorbed $N(CH_3)_3$ molecules can be removed from the surface without thermal decomposition after heating to 300 °C in a vacuum. In the presence of O_2, $N(CH_3)_3$ decomposes thermally at 230 °C. With photoirradiation in the presence of O_2, the adsorbed $N(CH_3)_3$ decomposes and forms $CO_{2(g)}$, $NCO_{(a)}$, $HCOO_{(a)}$, and surface species containing C═N or NH_x groups. $CH_3O_{(a)}$ is unlikely to be the reaction intermediate for the $HCOO_{(a)}$ formation. O_2 participates in the $NCO_{(a)}$ and $HCOO_{(a)}$ formation, i.e., incorporates its O into $NCO_{(a)}$ and $HCOO_{(a)}$. Upon photoirradiation of $N(CH_3)_3$ on TiO_2 in the presence of H_2O and O_2, a larger percentage of $N(CH_3)_3$ is consumed, compared to the case with only O_2. H_2O also plays a role in the $HCOO_{(a)}$ formation, as suggested by using $^{18}O_2$.

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