# Structural Investigation of the Hydrolysis–Condensation Process of Titanium Alkoxides $Ti(OR)_4$ (OR = $OPr^i$, OEt) Modified by Acetylacetone. 2. From the Modified Precursor to the Colloids

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The modified precursor $Ti(OPr^i)_3acac$ (acac = acetylacetonate) has been successfully used to prepare, via a sol–gel route, stable $TiO_2$-based colloids over a wide pH range. The hydrolysis–condensation process was investigated by using infrared, $^1H$ NMR, and X-ray absorption spectroscopies (XANES–EXAFS). The alkoxy groups are quickly removed during the hydrolysis while acetylacetonato groups still remain bound to titanium even when large amounts of water are present. The final colloids show structural data close to $TiO_2$ anatase. However, due to the presence of acetylacetonato groups, they exhibit quite unusual photochemical properties.

## Introduction

$TiO_2$-based colloidal solutions are of great interest for their photochemical properties.[1,2] Under irradiation, $TiO_2$ particles act as microphotoelectrodes, and chemical reactions can occur at the oxide–solvent interface. Two kinds of preparation have been described for these solutions: (i) $TiO_2$ powders can be dispersed in a solvent. The particle size is usually large in this case, and part of the incident light is scattered. (ii) $TiO_2$ particles have also been grown from solution by using a molecular precursor via hydrolysis–condensation process, usually resulting in small particles. However, $TiO_2$ precursors like titanium chloride or titanium alkoxides are quite sensitive to water, and control of the hydrolysis–condensation reactions to stabilize the colloidal particles is difficult to achieve.

Colloidal solutions of $TiO_2$ for photochemical studies have been prepared from titanium chloride $TiCl_4$[3] and titanium isopropoxide $Ti(OPr^i)_4$.[4] The hydrolysis is performed in acidic medium ($1.5 < pH < 3$) to prevent precipitation of $TiO_2$ particles. The final colloids have a hydrodynamic radius around 60 Å in the case of $TiCl_4$ and 200 Å in the case of $Ti(OPr^i)_4$. The optical bandgap is 3.2 eV, so they absorb only UV light.[5]

To stabilize colloidal particles, a modified precursor can be used. The substitution of alkoxy groups by less hydrolyzable groups such as $\beta$-diketones slows down the hydrolysis–condensation rates and allows better control of the size of the final particles.[6] Stable $TiO_2$-based colloids have been prepared by using a new precursor, $Ti(OPr^i)_3acac$, derived from the modification of titanium isopropoxide by acetylacetone. The colloidal solutions are yellow and remain stable over a wide pH range from 1 to 10. The presence of $\beta$-diketones surrounding Ti sites has shifted the optical absorption to longer wavelengths. The characterization of the modified precursor and the effect of the dilution with alcohol have already been described in part 1.[7] $Ti(OPr^i)_3acac$ is a monomeric species. The titanium ion is 5-fold coordinated. The dilution of this precursor in ethanol leads to the substitution of isopropoxy groups by ethoxy groups and then to the formation of oligomeric species in equilibrium with the monomers. This paper presents a structural investigation of the hydrolysis process. The first steps of the process have been followed by infrared, $^1H$ NMR, XANES, and EXAFS spectroscopies. The final colloidal solutions have been studied by quasi-elastic light-scattering, XANES, and EXAFS spectroscopies.

## Experimental Section

The modified precursor $Ti(OPr^i)_3acac$ is prepared by mixing, under magnetic stirring, acetylacetone with titanium isopropoxide in a 1/1 molar ratio. The isopropyl alcohol formed during the reaction is not removed. Then 5 mmol of this precursor is diluted in 25 mL of ethanol. This alcohol has been preferred to isopropyl alcohol because it leads to more stable colloids. The colloids are formed by hydrolyzing with 25 mL of water. The water is added to the solution with an automatic syringe in 2.5 h. The final concentration in titanium is 0.1 M, and the composition corresponds to 86 mol of ethanol and 275 mol of water per mole of titanium. The pH of the water has been adjusted by using HCl, $HNO_3$ or NaOH.

Infrared experiments were performed on a 580 Perkin-Elmer spectrometer with KRS5 disks. NMR spectra were recorded on a AM250 Bruker spectrometer. The samples have been diluted in a $CCl_4/CDCl_3$ mixture. X-ray absorption experiments were done at room temperature at LURE (Orsay, France). Experimental conditions and data analysis have already been described.[8] Quasi-elastic light-scattering measurements have been performed by using Malvern K 7025 equipment. Electron spin resonance spectra were recorded on a Varian E09 spectrometer. A Bruker NMR gaussmeter was used to measure the magnetic field with diphenylpicrylhydrazyl (DPPH) as a standard. X-ray experiments have been done on powdered samples using a Philips PW 1050/25 diffractometer.

## Results and Discussion

**Partial Hydrolysis.** The hydrolysis process was followed by using infrared, $^1H$ NMR, and X-ray absorption spectroscopies (XANES–EXAFS) for $H_2O/Ti$ ratios from 1 to 10. The presence of solvent was minimized to get clear infrared and NMR spectra: all the experiments have been done with a $Ti(OPr^i)_3acac/Pr^iOH/EtOH$ mixture (1/1/3

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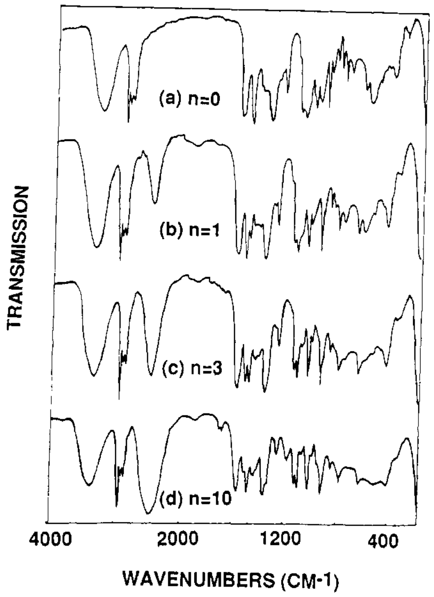

**Figure 1.** Evolution of the infrared spectra during the hydrolysis process ($n$ = $D_2O/Ti$).

ratio) as a starting solution.

The hydrolysis process was studied by infrared spectroscopy using deuterated water. It avoids the presence of the band due to the angular deformation of the water molecules around 1600 $cm^{-1}$, where the $\nu$(C–O) and $\nu$(C–C) bands of the acetylacetonato groups are found. The evolution of the infrared spectra is represented in Figure 1 for different $n$ = $D_2O/Ti$ ratios. Several interesting points should be noted: (i) The bands at 1100, 1020, 925, 845, and 765 $cm^{-1}$ progressively disappear. They correspond to ethoxy (1100 and 925 $cm^{-1}$) and isopropoxy (1010, 845, and 765 $cm^{-1}$) groups bound to titanium. It seems tht for $n$ = 3 only a few alkoxy groups remain bound to titanium. (ii) The bands in the 1400–1600-$cm^{-1}$ range, characteristic of acetylacetonato groups bound to titanium, still remain intense during the hydrolysis process. In fact, it should be noted that the band at 1520 $cm^{-1}$ ($\nu$(C–C)) disappears while a new band appears at 1500 $cm^{-1}$. This shift to lower frequencies could be due to the substitution of the acidic proton of acetylacetonato groups by a deuterium. (iii) Two new bands appear at 1700 and 1720 $cm^{-1}$ when 3 mol of $D_2O$ is added per titanium. They increase with the amount of water. They are characteristic of free acetylacetone (ketone form) and reveal a partial hydrolysis of some acetylacetonato groups. (iv) For a $D_2O/Ti$ ratio greater than 10, the band at 600 $cm^{-1}$, due to Ti–O(R) stretching vibrations (R = $Pr^i$, Et), disappears while broad bands are developing between 400 and 700 $cm^{-1}$ that are characteristic of the formation of a Ti–O–Ti network.

The infrared study shows that the addition of 3 mol of water per mole of modified titanium alkoxide leads to complete hydrolysis of the alkoxy groups while acetylacetonato groups just begin to hydrolyze. After the addition of 10 mol of water, the hydrolysis of these groups is still incomplete while condensation has already started.

The same process was followed by $^1H$ NMR. Figure 2 represents the spectrum of a $Ti(OPr^i)_3acac/Pr^iOH/EtOH$ solution (1/1/3 ratio) before and after hydrolysis. A previous study of the starting solution suggested the presence of several species (monomers and oligomers) in equilibrium.[7] The peaks at 1.93 and 2.04 ppm ($CH_3$ (acac)) and at 5.52, 5.54, and 5.56 ppm ($CH$ (acac)) were assigned to monomeric species while the peaks at 1.97 ppm ($CH_3$ (acac)) and 5.50 ppm ($CH$ (acac)) may correspond to oligomeric species in exchange. The addition of 0.5 mol of $D_2O$ per mole of titanium (Figure 2b) leads to some modifications of the starting spectrum: (i) The peaks at 1.97 and 5.50 ppm completely disappear, while all the other peaks corresponding to acac groups remain visible. It seems that the exchange between the species stops as soon as some water is added to the solution. (ii) The nonresolved bands at 3.85 ppm and 4.05 ppm corresponding to bound ethoxy ($CH_2$) and isopropoxy ($CH$) groups in exchange with free alcohol molecules disappear while resolved multiplets at 3.65 and 4.00 ppm due to free ethanol and isopropyl alcohol appear. The exchange between bound alkoxy groups and free alcohol molecules does not seem to occur any longer within the NMR time scale.

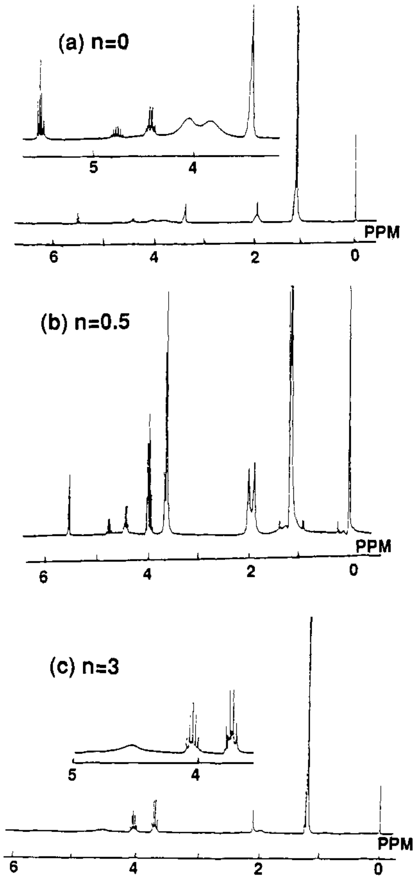

**Figure 2.** Evolution of the $^1H$ NMR spectra during the hydrolysis process ($n$ = $D_2O/Ti$).

These experimental data can be explained as follows. According to the proposed structural assignment for the monomeric species $Ti(OR)_3acac$, the OR group in the trans position with respect to acac group is much more labile than the OR groups in the cis position[7] and thus should hydrolyze first to give the $Ti(OR)_2(OH)acac$ species. OH groups can easily form bridges, and the presence of an OH group should move the equilibrium between monomers and oligomers toward the formation of oligomeric species leading to a dimerization of the compound with an OH and an OR group as bridging ligands. The Ti–OH–Ti bond is then strong enough to avoid any dissociation and exchange.

The peaks due to bound alkoxy groups rapidly disappear when water is added, and for 3 mol of $D_2O$ per titanium (Figure 2c), the hydrolysis process is almost complete. The hydrolysis of acetylacetonato groups starts for 2 mol of $D_2O$ per mole of titanium. Peaks corresponding to free acetylacetone appear at 2.05 ppm ($CH_3$) and 5.60 ppm (CH) for the enol form and 2.25 ppm ($CH_3$) for the ketone form.

This NMR study is in agreement with the infrared results and shows clearly that alkoxy groups are hydrolyzed

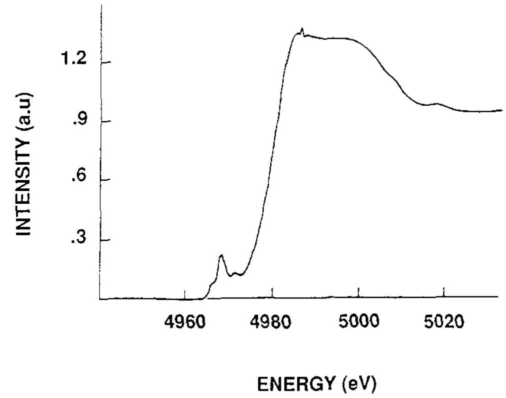

**Figure 3.** Ti K-edge XANES spectrum of the hydrolyzed solution ($H_2O$/Ti = 3).

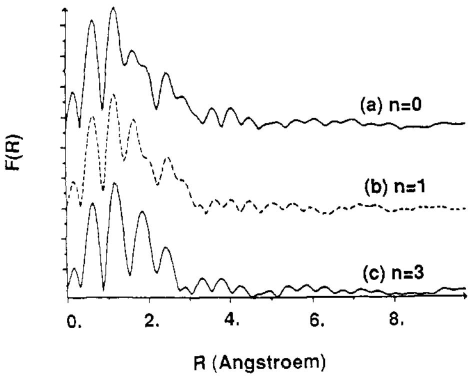

**Figure 4.** Evolution of the radial distribution function during the hydrolysis process ($n$ = $H_2O$/Ti).

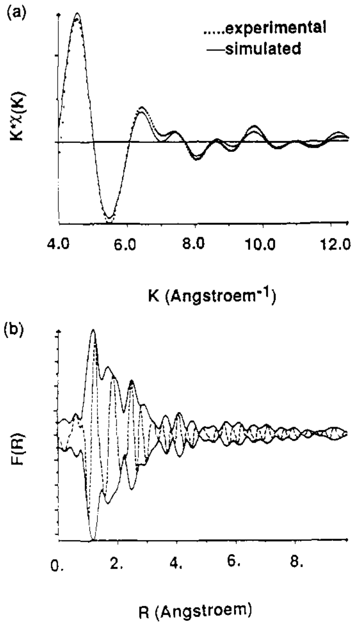

**Figure 5.** (a) Ti K-edge filtered EXAFS spectrum and (b) radial distribution function for the hydrolyzed solution ($H_2O$/Ti = 3).

**Table I. Fitted EXAFS Parameters for the Hydrolyzed Solution Prepared from Ti(OPr$^i$)$_3$acac ($H_2O$/Ti = 3)**

| | $N$ | $R$, Å | $\sigma$, Å | $E_0$, eV | $\Gamma$, Å$^{-2}$ | $\rho$, % |
|---|---|---|---|---|---|---|
| Ti–O | 1.4 | 1.77 | 0.071 | 4985 | 1.24 | 6.8 |
| | 1.9 | 1.94 | 0.071 | 4985 | 1.24 | |
| | 1.6 | 2.44 | 0.071 | 4985 | 1.24 | |
| Ti–C | 5.8 | 2.99 | 0.073 | 4973 | 1.24 | |
| Ti–Ti | 2.3 | 3.19 | 0.140 | 5010 | 1.24 | |

before acetylacetonato groups. Furthermore it appears that the hydrolysis of the alkoxy groups is almost complete when more than 3 mol of water is added to the starting solution while only partial hydrolysis of the acetylacetonato groups takes place even for large amounts of water ($n$ > 10).

To get more precise details concerning the structure of the different hydrolyzed and/or condensed species, X-ray absorption experiments have been done on the same solutions (Ti(OPr$^i$)$_3$acac/Pr$^i$OH/EtOH in a 1/1/3 ratio). Titanium K-edge XANES spectra of solutions hydrolyzed with 1 and 3 mol of water have been recorded. Both spectra are roughly identical (Figure 3). A triplet appears before the edge with three peaks centered at 4965.8, 4968.0, and 4971.4 eV. The spectrum of the starting solution has previously been published.[7] It exhibits only a single peak at 4968.0 eV with a shoulder at 4966.2 eV. These features were assigned to the presence of a mixture of 5- and 6-fold coordinated species. The triplet that appears as soon as some water is added to the starting solution clearly shows that only 6-fold coordinated species remain in solution. The formation of dimers suggested by the NMR results is in perfect agreement with such data.

EXAFS spectra of both solutions hydrolyzed with 1 and 3 mol of water per mole of titanium have been recorded. The radial distribution functions of these spectra as well as that of the starting solution are represented in Figure 4. The data for the starting solution have already been analyzed.[7] The first peak a low $R$ values is due to noise. The two following peaks in the 1.5–2-Å range correspond to short and long Ti–O distances. The short distances are due to terminal alkoxy groups while the long ones correspond to bridging alkoxy groups and acetylacetonato groups. The less intense peak, beyond 2 Å, was assigned to some Ti–C distances. Adding water strongly modifies this radial distribution function. The peak due to the short Ti–O distances seems to remain constant. The peak corresponding to long Ti–O distances decreases in intensity and slightly shifts to lower $R$, values while a new peak appears at higher $R$ values. The peak due to Ti–C distances is still visible, while a new peak at higher $R$ values also appears. The EXAFS spectrum corresponding to the solution hydrolyzed with 3 mol of water per mole of titanium was fitted (Figure 5), and the results are summarized in Table I. Two points are quite interesting: the presence of three different Ti–O distances of 1.77, 1.94, and 2.44 Å and a Ti–Ti distance of 3.19 Å. This last value clearly shows that stable oligomeric species are formed during the hydrolysis process. The distance could correspond to octahedra sharing edges as in $TiO_2$ anatase and should be related to the dimerization previously assumed to occur as the first step of the condensation process. The assignment of the Ti–O distances is not easy because different species are certainly present in solution. Assuming a complete hydrolysis of alkoxy groups, hydroxyls, acetylacetonato groups, water molecules, or bridging oxygens are expected to surround titanium ions. The short Ti–O distances of 1.77 Å should correspond to terminal OH groups.[8] The Ti–O distances of 1.94 Å could be assigned to acetylacetonato groups or bridging oxygens.[8] The long Ti–O distances of 2.44 Å are quite difficult to assign. They appear during the hydrolysis–condensation process and increase with the amount of water. They could be due to either bridging OH groups or $H_2O$ molecules coordinated to titanium.

X-ray absorption experiments show that stable oligomeric species are formed when water is added to the starting

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**Table II. Quasi-Elastic Light-Scattering Measurements on Colloidal Solutions**

| precursor | $n_d$ | $n_h$ | pH | $R_H$, Å |
|---|---|---|---|---|
| $Ti(OPr^i)_4$ | 37 | 1500 | 1.5 | 140 |
| $Ti(OPr^i)_3acac$ | 86 | 275 | 1.5 | 30 |
| | 86 | 275 | 7 | 60 |
| | 86 | 110 | 7 | 40 |
| | 34 | 275 | 1.5 | 55 |

**Table III. Ti K-Edge XANES Data of Colloidal Solutions**

| sample | preedge peaks, eV | edge peaks, eV | postedge peaks, eV |
|---|---|---|---|
| colloids, pH = 1.5 | 4965.6, 4967.8, 4971.2 | 4984.4 | 4999.5 |
| colloids, pH = 7 | 4965.8, 4968.2, 4971.4 | 4984.7 | 4998.6 |
| $TiO_2$ anatase | 4966.0, 4968.8, 4971.6 | 4984.5 | 5000.2 |

solution. It is difficult to derive precise structures for these species. Titanium ions are clearly in a 6-fold coordination. The octahedra seem to be strongly distorted with three different Ti–O distances and are bound together via their edges, according to the Ti–Ti distance value.

**Colloids.** The final goal of this work was to prepare stable $TiO_2$-based colloids. Such colloids can be obtained via the hydrolysis of the modified precursor $Ti(OPr^i)_3acac$. Dilution of this precursor in isopropyl alcohol leads to some precipitation after hydrolysis. The use of ethanol allows the preparation of stable colloids. Hydrolysis can be performed over a wide range of pH, from 1 to 10. When the colloids are prepared from titanium isopropoxide, they are stable only below pH = 3.

Due to the large amount of solvent, infrared and $^1H$ and $^{13}C$ NMR spectroscopies are useless as a source of structural information. These colloids were studied by quasi-elastic light scattering to measure particle size and by X-ray absorption spectroscopy to characterize the environment of titanium ions.

Several colloidal solutions have been prepared with different dilution ratios ($n_d$ = EtOH/Ti), hydrolysis ratios ($n_h$ = $H_2O$/Ti), and hydrolysis pH. A colloidal solution has also been obtained from the hydrolysis of titanium isopropoxide and was used as a reference. The results provided by quasi-elastic light scattering are summarized in Table II. The colloids prepared from titanium isopropoxide $Ti(OPr^i)_4$ have a hydrodynamic radius of around 140 Å while those prepared from the modified isopropoxide $Ti(OPr^i)_3acac$ exhibit much smaller radii, ranging from 30 to 60 Å. This radius increases with the hydrolysis ratio and decreases with the dilution ratio. In acidic pH, particles are smaller than at higher pH.

X-ray absorption experiments were done on two colloidal solutions. Their characteristic were the following: solution A, $n_d$ = 86, $n_h$ = 275, pH = 7; solution B, $n_d$ = 86, $n_h$ = 275, pH = 1.5. For solution B, nitric acid was used to adjust the pH value instead of hydrochloric acid to avoid the high absorption of Cl atoms at the Ti K edge. Ti K-edge XANES spectra of the two solutions are similar and close to the XANES spectrum of $TiO_2$ anatase (Figure 6). The energy values of the different peaks are summarized in Table III. The Ti ions in these colloids are 6-fold coordinated, and the oxygen environment should be close to that in anatase.

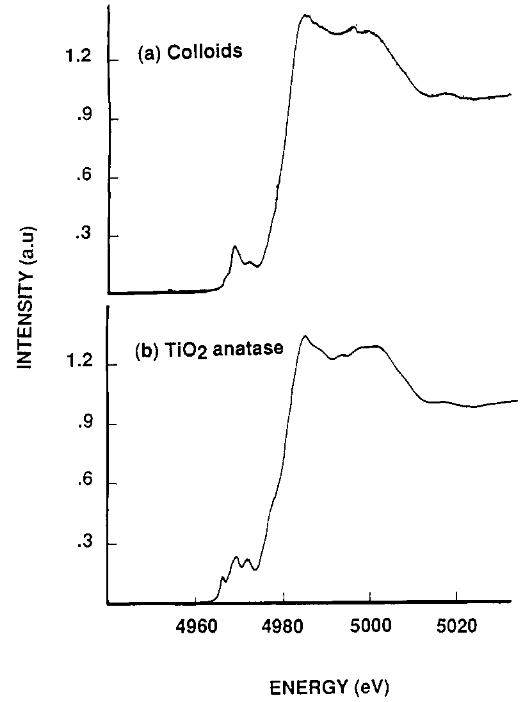

**Figure 6.** Ti K-edge XANES spectra of (a) colloids prepared from $Ti(OPr^i)_3acac$ at pH = 7 and (b) $TiO_2$ anatase.

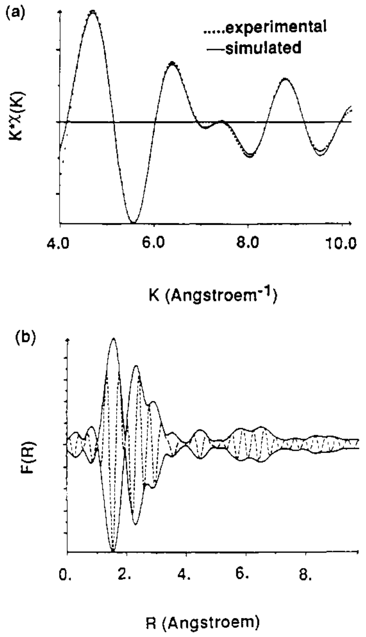

**Figure 7.** (a) Ti K-edge filtered EXAFS spectrum and (b) radial distribution function of colloids prepared from $Ti(OPr^i)_3acac$ at pH = 1.5.

**Table IV. Fitted EXAFS Parameters of Colloidal Solutions Prepared at pH = 1.5 and 7**

| soln | $N$ | $R$, Å | $\sigma$, Å | $E_0$, eV | $\Gamma$, Å$^{-2}$ | $\rho$, % |
|---|---|---|---|---|---|---|
| pH = 7 | | | | | | |
| Ti–O | 4.8 | 2.01 | 0.081 | 5003 | 1.9 | 1.0 |
| Ti–Ti | 5.6 | 2.98 | 0.106 | 4965 | 1.9 | |
| pH = 1.5 | | | | | | |
| Ti–O | 4.4 | 1.90 | 0.092 | 4991 | 1.2 | 1.0 |
| Ti–Ti | 6.0 | 2.93 | 0.115 | 4964 | 1.2 | |

The EXAFS spectra of the two solutions have also been recorded at the Ti K edge. The absorption of oxygen atoms at this energy is rather important. The large amount of solvent (water and ethanol) and thus of oxygen atoms in these colloidal solutions leads to noisy spectra. Nevertheless, some structural data have been extracted. Figure 7 represents the fitted EXAFS spectrum and the radial distribution function for solution A. The fitted parameters for both solutions are summarized in Table IV. In both cases, only one Ti–O distance (1.96 Å for A and 2.01 Å for B) and one Ti–Ti distance (2.93 Å for A and 2.98 Å for B) have been found. Ti–O distances could correspond to μ-oxo bridges (1.93 and 1.96 Å in $TiO_2$ anatase)

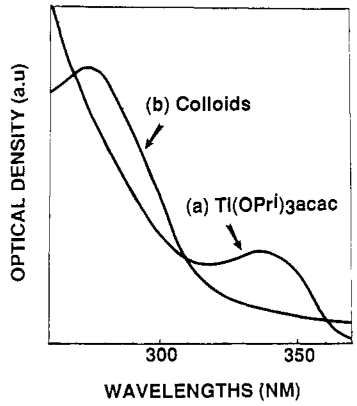

**Figure 8.** Optical spectra of (a) $Ti(OPr^i)_3acac$ and (b) colloids prepared from this precursor at pH = 1.5.

or acetylacetonato groups (2.00 Å in $Ti(OPr^i)_3acac$). Ti–Ti distances are slightly shorter than those observed in $TiO_2$ anatase (3.04 Å). They correspond to $TiO_6$ octahedra sharing edges.

The presence of acac groups coordinated to Ti can be confirmed by UV–visible spectroscopy (Figure 8). Free acetylacetone exhibits a band at 270 nm due to the $\pi \rightarrow \pi^*$ transition absorption. This band shifts toward longer wavelengths when acetylacetone reacts with a metallic ion to form a complex.[9] The $\pi \rightarrow \pi^*$ transition appears at 325 nm in $Ti(OPr^i)_3acac$ and is responsible for the yellow coloration of the precursor. This band decreases in the colloids, and a new one appears at 270 nm assigned to the presence of free acetylacetone in the solution. This has to be related to the hydrolysis of some acac groups as previously shown by infrared and $^1H$ NMR spectroscopies. Nevertheless, the colloids still appear yellow: acac groups are still present in the environment of titanium ions.

These colloids are photosensitive and turn blue or pink under visible light irradiation depending on the pH value of the hydrolyzing water. The study of the photochemical properties will not be described in detail here. However, some interesting structural information can be obtained by using these properties. The change in color of the colloidal solutions under irradiation is due to the reduction of some $Ti^{4+}$ to $Ti^{3+}$ ions. The color depends on the crystal field surrounding the $Ti^{3+}$ ions, and thus an electron spin resonance (ESR) study of the $Ti^{3+}$ species can provide information concerning the symmetry of Ti sites. The ESR spectra of the colloidal solutions prepared at pH = 1.5 and pH = 7 have been recorded at 100 K. The pink species (pH = 1.5) are characterized by an orthorhombic symmetry ($g_1 = 1.91, g_2 = 1.97, g_3 = 1.99$). The blue species (pH = 7) correspond to an axial symmetry ($g_\perp = 1.93, g_\parallel = 1.99$). These last parameters are close to those of $Ti(acac)_3$ and could correspond to a trigonal distortion of the site arising from the presence of an acetylacetonato group bound to titanium.[10] The $g$ parameters of the pink species are close to those found for $TiO_2$ crystalline phases (anatase or rutile)[11,12] and should reflect a tetragonal distortion of the $Ti^{3+}$ sites: acac groups are apparently no longer bound to titanium. Acac groups should stabilize the $Ti^{3+}$ species because of $\pi$ electronic delocalization. Under irradiation, these sites are first photoreduced and the colloidal solution turns blue. When the hydrolysis is performed in an acidic medium, acetylacetonato groups seem to be removed more easily. The remaining Ti sites are similar to those in $TiO_2$. The colloidal solution turns pink under irradiation. These results are in agreement with EXAFS data. Ti–O distances were assigned to $\mu$-oxo bridges or acetylacetonato groups. The colloidal particles can be described as having a bulk structure similar to $TiO_2$ anatase with some acetylacetonato groups bound to Ti sites present at the surface. The number of acac groups may vary with the pH at which the hydrolysis is performed and thus modify the photoreactivity of the solution.

Powders have been obtained from the colloidal solutions after evaporation of the solvent under vacuum. They have been characterized by infrared spectroscopy, chemical analysis and X-ray diffraction. Results do not seem to depend strongly on the pH used for the hydrolysis process. Infrared spectra clearly exhibit bands due to acetylacetonato groups bound to titanium at 1580 and 1530 $cm^{-1}$ ($\nu$(C–O) + $\nu$(C–C)), at 1420 and 1360 $cm^{-1}$ ($\delta(CH_3)$), at 1280 $cm^{-1}$ ($\nu(C{-}CH_3)$), and at 1030 $cm^{-1}$ ($\rho(CH_3)$). Bands due to alkoxy groups are no longer present in the 1000–1200-$cm^{-1}$ range. Broad bands below 900 $cm^{-1}$ are characteristic of a Ti–O–Ti network.

Assuming that C atoms belong to acetylacetonato groups, chemical analysis leads to the following formula: $TiO_{1.85}(acac)_{0.3}\cdot 1.5H_2O$. The samples are amorphous by X-ray diffraction. After a thermal treatment at 80 °C for 40 h, the diffraction patterns show broad peaks characteristic of crystalline $TiO_2$ anatase. These results on the powders are in agreement with the proposed structure of the colloidal particles.

## Conclusions

The hydrolysis–condensation process of a modified titanium alkoxide $Ti(OPr^i)_3acac$ was investigated. For a $H_2O/Ti$ ratio of 1, the alkoxy group in a trans position relative to an acac group is removed. This leads to the formation of dimeric species with OH bridges. The remaining alkoxy groups are removed for $H_2O/Ti$ greater than 1, and the hydrolysis is almost complete for a $H_2O/Ti$ ratio of 3. Some acetylacetonato groups start to be hydrolyzed for a ratio of 2. However, the reaction is incomplete and acetylacetonato groups still remain bound to titanium even when hydrolysis is performed with a large excess of water. $^1H$ NMR and X-ray absorption at the Ti K-edge appear to be quite complementary techniques to follow the first steps of hydrolysis. The first technique provides information on the organic groups and thus on the hydrolysis process, while the second one give details on the modification of the environment of the metallic ion and is much more sensitive to the condensation process.

Extended hydrolysis leads to the formation of small particles from 30 to 60 Å in radius. XANES and EXAFS provide interesting structural information on these colloidal solutions. The structure of the particles appear close to that of $TiO_2$ anatase. However, they exhibit specific photochemical properties. These colloids are easily photoreduced, and the photogenerated $Ti^{3+}$ ions can be used as internal probes to investigate the local symmetry of titanium sites in these colloids. ESR studies, performed on the irradiated colloidal solutions, show the presence of two kinds of Ti sites. Some sites are similar to $TiO_2$ sites, but for some others, acetylacetonato groups are coordinated to titanium. The colloidal particles can be described as $TiO_2$ anatase particles with acetylacetonato groups bound to Ti surface sites. The presence of these groups leads to interesting photochemical properties that will be described subsequently.

**Registry No.** $Ti(OPr^i)_3acac$, 15701-48-1.

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