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Esterification kinetics in titanium isopropoxide-acetic acid solutions

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FTIR observation has been used to analyze the reaction between titanium isopropoxide and acetic acid under a variety of conditions. Isopropyl acetate ester forms in these mixtures and serves as an indicator of the extent of condensation between the titanium precursors. Condensation occurs to a gradually increasing extent to form a broad spectrum of titanium oxo-acetate polymers. The temperature dependence of the time to reach observable precipitation in these solutions has also been mapped out. The activation energy for this process was found to be 0.7 eV. The precipitation times have a direct bearing on how these solutions can be used when making a wide variety of titanium containing sol-gel solutions.

1. Introduction

The sol-gel chemistry is an important method for preparing chemically homogenenous coatings and powders with a wide variety of useful applications, as evidenced by the many conference and symposia devoted to the topic [see for example references 1–9]. Sol-gel processes usually involve various metal alkoxide molecules that are hydrolyzed under controlled conditions and then subsequently reacted to condense with each other to form metal-oxygen-metal bridging units.

Titanium is a very important constituent of many compositions that are attempted using the sol-gel process. It helps confer high refractive index when used as an additive into optical glasses [10, 11]. It is also an important constituent for a wide variety of dielectric, ferroelectric, and other electrically active compounds, especially the perovskite titanates and their solid solutions [12]. When trying to incorporate titanium into a sol-gel solution, it is common to use one of several commercially available alkoxides and to reduce its reactivity by modifying it with some appropriate chemical modifier. One of these precursors, titanium isopropoxide (TIP), is the focus of the present study. Of the many available modifiers, acetic acid has been used in the present work. Acetic acid (HOAc) is a popular modifier partly because it can easily dissolve a wide variety of different precursor molecules, helping enable the creation of a multitude of multi-cation solutions [13–15]. However, these chemistries are sometimes touchy because the acetic acid can drive an esterification reaction with any alcohol that is present, thus liberating water into the solution.

The esterification reaction can present some potential problems for sol-gel routes because, if the reaction is not controlled, the water liberated can cause precursor condensation reactions (and ultimately precipitation) in the solution. This is especially important when TIP-HOAc mixtures are *heated* in order to dissolve other precursor components (for example when using the "inverted mixing order" chemistry for making PZT [15]). Thus, the gradual generation of water by the esterification reaction (during subsequent processing) can put restrictions on the time and temperature that might be used for carrying out these reactions. On the other hand, it has been pointed out that the esterification reaction is an efficient method for introducing water *homogeneously* into a solution and therefore avoiding the problems associated with mixing irregularities [16, 17]. Since the water generation (and therefore the solution hydrolysis) is a critical variable in sol-gel processing, it is important to understand how this varies with time and temperature.

Whether the esterification reaction is driven intentionally or not, it is interesting to understand the extent to which TIP-HOAc mixtures react and the amount of water that might be generated in these processes. Thus, the present work studies these reactions using FTIR to distinguish the characteristic C=O peaks from the ester that is the by-product of the reaction. With careful calibration, it has been possible to measure the kinetics of the esterification reaction.

2. Background

As a foundation for understanding the esterification behavior in general, it is important to examine the earlier stages of reactions between TIP and HOAc. These reactions can be described by three basic stages. Stage one covers the ligand exchange and modification of the TIP. Stage two covers the gradual esterification process

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during the time when all oligomers remain soluble. The final stage is the precipitation and/or crystallization of reaction products.

As stated above, it is well known that acetate groups can replace isopropoxy groups, thus creating a soluble species with much lower reactivity than the starting TIP [13, 17–19]. In fact, it has been shown that up to *two* acetate groups will be easily accepted in this exchange process [18, 20, 21]. The liberated isopropoxy groups enter solution as isopropanol according to this reaction:

$$\text{Ti-O}i\text{Pr} + \text{HOAc} \leftrightarrow i\text{PrOH} + \text{Ti-OAc} \qquad (1)$$

(Note that in this and subsequent reactions, only one of the four titanium-bound ligands is shown to give a schematic representation of the reaction.) If fewer than two HOAc molecules are provided for this reaction, then they react (nearly) completely away. However, if more than two HOAc are provided to the solution, then two are reacted away to form $\text{Ti(O}i\text{Pr)}_2\text{(OAc)}_2$ molecules, which stay in solution with a mixture of iPrOH and the remaining HOAc [21]. This modification process is quite rapid and exothermic in nature.

The second stage of the process is the reaction of isopropoxy and acetate ligands to form ester in solution. The simplest possibility is a direct esterification reaction between the isopropanol and acetic acid according to:

$$i\text{PrOH} + \text{HOAc} \leftrightarrow i\text{PrOAc} + \text{H}_2\text{O} \qquad (2)$$

Water produced according to reaction (2) would be able to hydrolyze Ti-bound isopropyl groups leaving terminal hydroxy groups which can condense forming, Ti-O-Ti, oxo-bridges. However earlier experimental data suggest that some type of "transesterification" is more likely to occur [22, 23]. In this case, titanium bonded isopropyl and acetate ligands can participate in a condensation reaction, also yielding isopropyl acetate as a byproduct:

$$\text{Ti-O}i\text{Pr} + \text{Ti-OAc} \leftrightarrow i\text{PrOAc} + \text{Ti-O-Ti} \qquad (3)$$

This esterification reaction results in the direct formation of a Ti-O-Ti bridge. Related reactions can occur between free acetic acid and bound isopropyl groups or free alcohol and bound acetate:

$$\text{Ti-O}i\text{Pr} + \text{HOAc} \leftrightarrow i\text{PrOAc} + \text{Ti-OH} \qquad (4)$$

$$\text{Ti-OAc} + i\text{PrOH} \leftrightarrow i\text{PrOAc} + \text{Ti-OH} \qquad (5)$$

These related reactions yield highly reactive Ti-OH groups that will rapidly condense to form Ti-O-Ti bridges. In all combinations, the production of the ester will ultimately create oxygen linkages between titanium atoms, even if only through the subsequent rapid reaction of the water (as shown in Equation 2) or of hydroxyls (as shown in Reactions 4 and 5). No matter which reaction pathway is fastest, there will be only one Ti-O-Ti bridge formed for every ester molecule formed. Because of the high reactivity of the titanium oligomers with water, it is unlikely that these solutions contain any appreciable quantity of free water. Instead, the extent of the ester formation will monitor the extent of condensation between the titanium molecules.

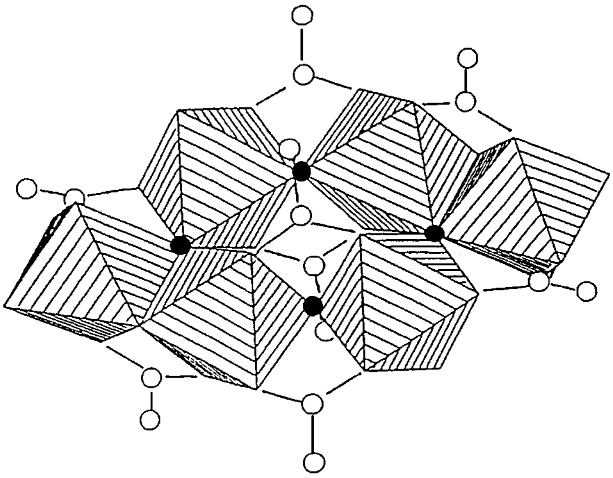

Figure 1 Titanium oxo-bonded ring hexamer molecule found in 1 : 2 TIP : HOAc solutions after aging. Open circles show positions of carbon atoms in bridging bidentate acetate groups. Filled circles show positions of bridging oxygen atoms. Figure adapted from reference [26].

If reactions are carried out for long enough time (usually several days at room temperature), then precipitation is observed in titanium alkoxide-acetic acid mixtures [22, 24–28]. Depending on the level of HOAc available in the starting solutions, then crystals of either $\text{Ti}_6\text{O}_4\text{(O}i\text{Pr)}_{12}\text{(OAc)}_4$ or $\text{Ti}_6\text{O}_4\text{(O}i\text{Pr)}_8\text{(OAc)}_8$ have been found. Fig. 1 shows a schematic representation of the second of these two molecules. In these molecules there are six octahedrally-coordinated titanium atoms and the ring is bound together with four oxo bridges (indicated by the black circles in the diagram). Of course, at early reaction times, the amount of ester produced cannot provide for the formation of significant quantities of these ring-structured molecules. Instead, it can be imagined that a wide variety of different molecules exist, including dimers, trimers, and chains of various length. Ultimately, these molecules can react to their most stable endpoint (the hexamer) and when their concentration reaches supersaturation, precipitation will occur.

The ability of the solution to reach the precipitation point (or conversely, the ability to prevent precipitation) depends on the rate of the esterification reaction. A recent NMR study has shown a nominal kinetic response for the ester production rate, whereby the average quantity of oxo-bridges per titanium atom was quantified [21]. It was found that after two days of reaction, the oxo/Ti ratio had reached a value of 0.47. Still, more than half of these oxo-bridges had been formed in the first five hours of reaction, indicating considerable slowing of the reaction with time. An earlier NMR study has also looked at the room temperature esterification kinetics at long times for low acetate modification levels (1 : 1 and 1 : 2), but did not quantify the ester concentrations (or titanium condensation levels) found [25]. Most data were gathered at times beyond 100 h and probably covered only the later stages of ester formation.

To date, no further details of the reaction kinetics at early times in this system have been deduced. In addition, other variables of direct impact upon the esterification reaction have not been studied at all, including composition and temperature dependences. Thus, the present study focuses on acquiring a better understanding of all aspects of the ester formation reaction in various TIP-HOAc mixtures, up until the point when precipitation occurs.

3. Experimental procedure

Fourier transform infra-red absorption (FTIR) measurements have been made on a variety of TIP-HOAc solutions, covering different mixing ratios, reaction temperatures, and reaction times. In all cases the solution samples have been measured in a ZnSe attenuated total reflection (ATR) cell using a Brucker IFS25 spectrometer. Titanium isopropoxide was pre-distilled before use, acetic acid was stored over molecular sieve, and all mixing, reactions, and storage were carried out under Ar gas.

In addition to the samples of direct interest, the FTIR peak positions and intensities were calibrated using a variety of *i*PrOH-HOAc mixtures, as well as solutions containing known, intentionally added, concentrations of isopropyl-acetate ester. Peak assignments and spectrum analysis are consistent with prior work [29–31]. The calibration runs are described in detail as part of the results section below. After giving the basis for ester concentration measurement using FTIR, the data from TIP-HOAc reactions are given. Finally, the data are discussed and compared with previous understanding about ester formation and titanium oligomer condensation in this system.

4. Results

Fig. 2 shows part of the FTIR spectra for four of the important pure constituent chemicals. From top to bottom, the lines are for HOAc, *i*PrOH, isopropyl-acetate ester, and TIP, where the lines have each been offset by unit increments to allow for easier discrimination of peak positions. Of course, because similar building blocks are used in all of the molecules, there are many similarities in various parts of the spectra. After intensive and careful analysis, the most useful quantifiable peaks were identified. These peaks lie at around 1250 and 1735 cm^{-1}. These intense peaks arise respectively from the C–O–C and C=O stretching vibrations in the ester molecule [30, 31]. The spectrum for acetic acid also has peaks in these areas, however, the shapes and intensities are different than for the ester molecule. In addition, these acetate group vibrations were found to be relatively unaffected when bonded with titanium. Both of these peaks were used here for quantification of the ester content of reacting solutions.

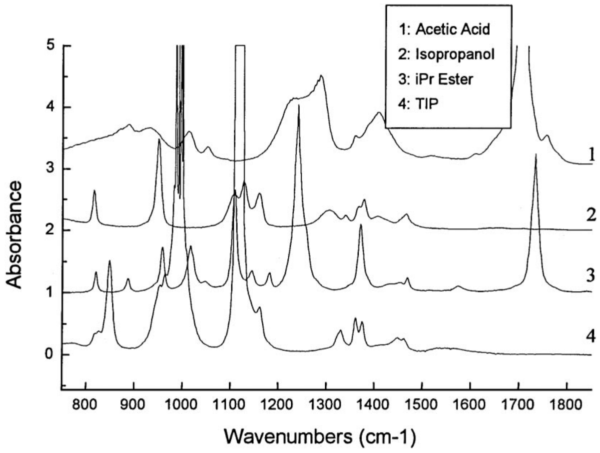

Figure 2 ATR-FTIR spectra from pure solutions of (from top to bottom) acetic acid, isopropyl alcohol, isopropyl acetate, and titanium isopropoxide. The curves have been offset upwards by one or more units to facilitate viewing.

Because of the known overlap between the ester and the free acetic acid, careful calibration solutions were prepared and measured. The main series used equal volumes of isopropanol and acetic acid, with increasing additions of isopropyl-acetate ester. Fig. 3 shows the peak near 1735 cm^{-1}, measured for each of these samples. The growth of intensity within the range 1720–1750 was used as a measure of the fraction of acetate groups that had been converted to ester molecules. Fig. 4 shows the corresponding spectra in the region around the 1250 cm^{-1} peak. In this region, the growth of intensity between 1200 and 1260 was used as a measure of the ester content in other solutions. Careful background subtraction and peak normalization was performed by establishing a baseline intensity on the sample with 0 percent ester content and then subtracting this intensity from the integrated intensity for other samples. Integration limits were [1720,1750] and [1200,1260] cm^{-1}, respectively. A calibration relationship was established based on the known samples described above. This calibration was then applied to the reacting samples by measuring the corresponding baseline in the starting solution and then subtracting this from the intensity integrated after a known reaction time.

These calibrations were applied to a mixture of undiluted TIP and acetic acid with molar ratio 1 : 4 that was heated at 80 °C for various times. This temperature was chosen because the reaction was known to proceed far enough that precipitation would occur shortly after one hour of heating. Aliquots of solution were removed at regular intervals and placed into a refrigerator until the continued heating of the remaining solution was completed, then FTIR data acquisition was commenced immediately. Fig. 5 shows the changes that occurred in the key spectral region. In addition to the expected changes that occurred near the 1250 and 1735 cm^{-1} ranges, there were other significant spectral evolution trends. Because of the number of data lines incorporated in Fig. 5, small arrows have been added to indicate these trends in intensity with increasing reaction time.

New features have appeared which are not associated with the pure starting solutions shown in Fig. 2 above. These are the two broad peaks around 1425 and 1575 cm^{-1} that are associated with bidentate acetate groups [30, 32, 33]. These result from bidentate acetate groups that have replaced isopropoxy groups in the first stage of the reaction. Further comments about changes to these peaks are given in the discussion section.

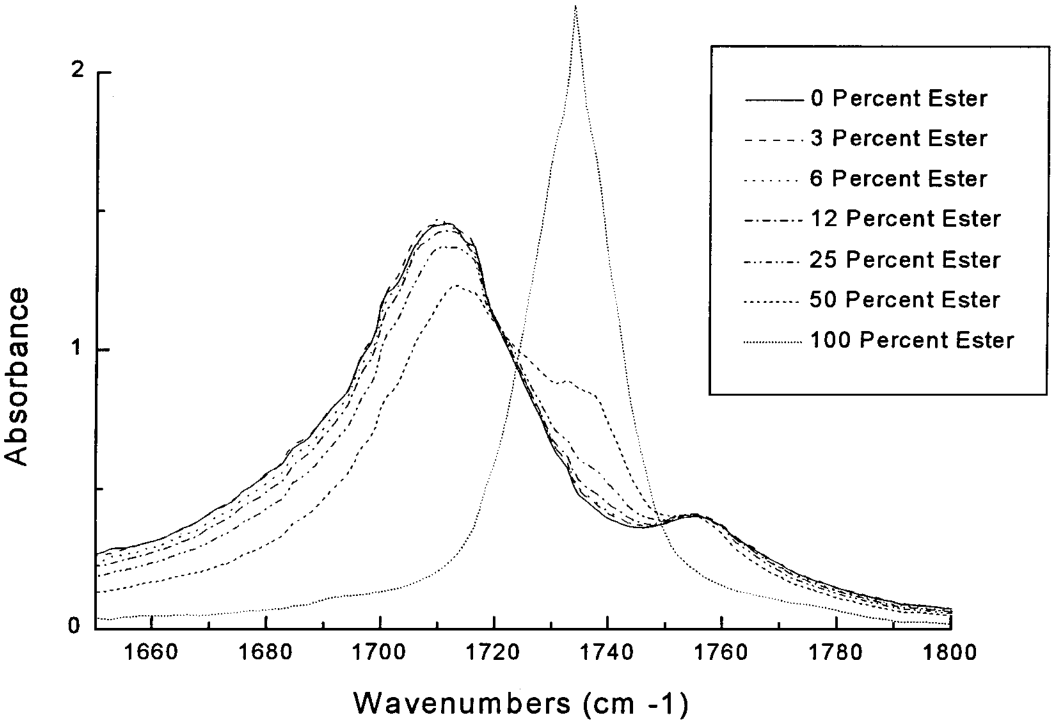

Figure 3 FTIR data for isopropanol-acetic acid-ester mixtures. Detail in the region surrounding the ester peak at 1735 cm^{-1}.

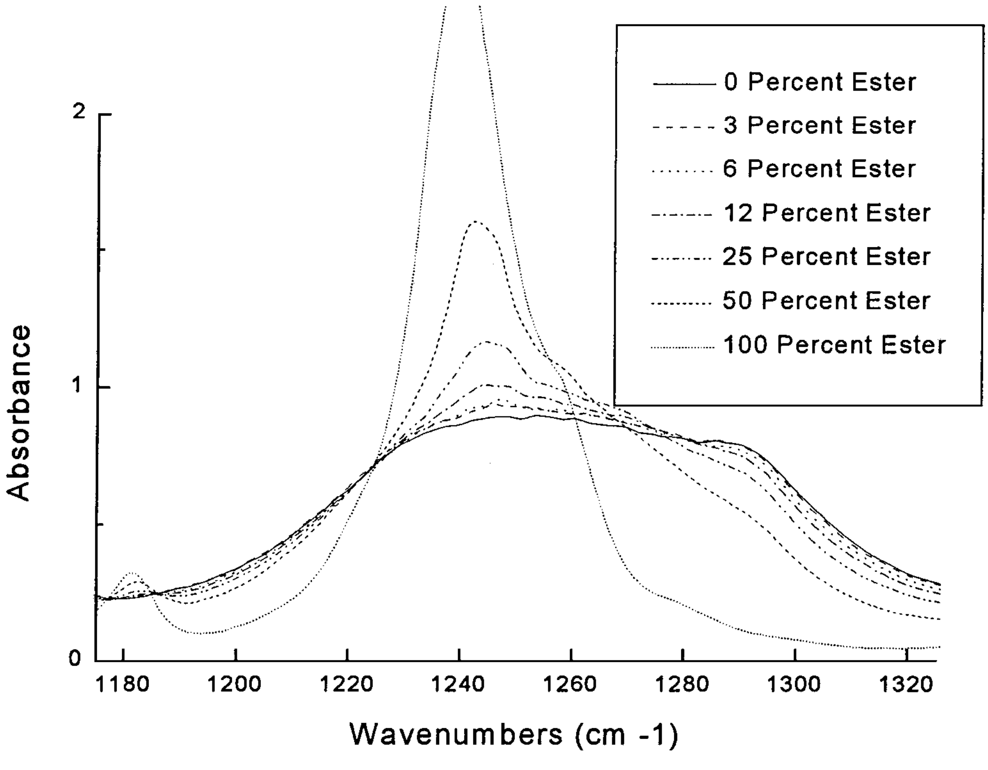

Figure 4 FTIR data for isopropanol-acetic acid-ester mixtures. Detail in the region surrounding the ester peak at 1250 cm^{-1}.

The spectra shown in Fig. 5 were analyzed using the procedure developed with the calibration solutions describe above. Peak intensities were integrated and from these values, the volume percent of ester in solution was calculated. Table I gives these measured ester concentrations. The agreement between ester concentrations measured using the two different FTIR peaks is quite good.

As condensation of the starting molecules progresses (and ester is produced as a result), the average titanium bonding environment will change. The resulting solution-average titanium oligomer, $TiO_R(OiPr)_{2-R}(OAc)_{2-R}$, can be described by the following reaction:

$$Ti(OiPr)_2(OAc)_2 \leftrightarrow TiO_R(OiPr)_{2-R}(OAc)_{2-R} + R\,iPrOAc \qquad (6)$$

The value R describes the extent to which the esterification and condensation has progressed in solution. R ranges from 0 (immediately after modification by the

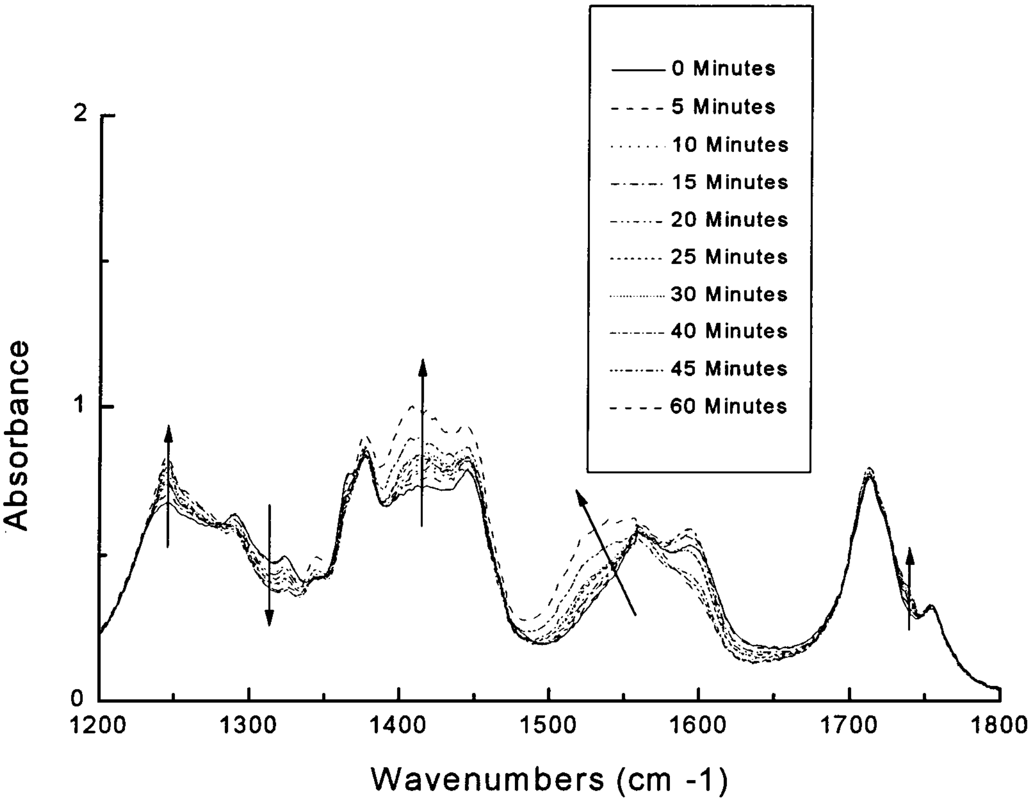

Figure 5 FTIR observation of 1 : 4 TIP : HOAc mixture heated for various times at 80 °C. Arrows show signifcant peak intensity changes with increasing time and are discussed in the text.

TABLE I Measured isopropyl acetate ester concentrations as a function of reaction time at 80 °C

Reaction time (min)	Volume percent ester (using peak around 1250 cm^{-1})	Volume percent ester (using peak around 1735 cm^{-1})
0	0[a]	0[a]
5	2.2	1.9
10	5.2	4.6
15	7.9	6.0
20	10.3	8.7
25	12.9	11.1
30	14.4	12.6
40	19.2	16.8
45	19.6	18.2
60	20.6	18.7

[a] Data are referenced to the ester content found in the as-mixed solution before heating and are believed accurate to within 15% of their measured values.

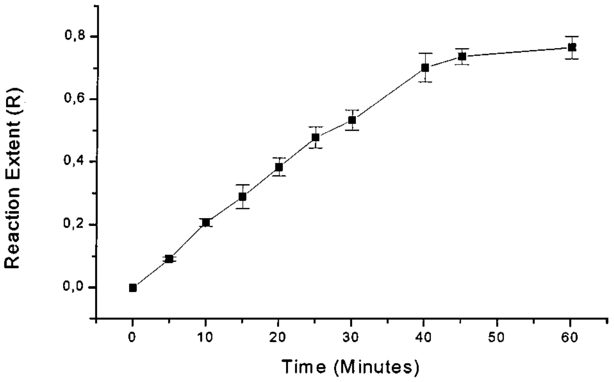

Figure 6 Level of condensation between titanium precursors deduced from the evolution of ester concentration in solution. *R* is defined as the number of moles of isopropyl ester formed per mole of TIP in the starting solution.

acetic acid) to 2 (for fully condensed titanium oxide particles). The bonded isopropoxy and aceto quantities are shown to maintain a constant ratio throughout the reaction, consistent with prior NMR work [21]. Using this reaction description, the ester content in solution (from Table I) can be used to deduce the level of condensation, *R*, and its variation with time. It should be noted that the value *R* also represents the average bridging oxygen to titanium atom ratio in solution. The *R* data for a solution heated at 80 °C are plotted in Fig. 6. The rate of ester formation is initially quite constant, and eventually nears saturation before precipitation occurs (around 75 min).

It is interesting now to focus on the temperature dependence of this ester formation reaction. As stated earlier, this is important because it sets bounds on time-temperature combinations to which these solutions can be exposed without complications. To investigate this effect, solutions were heated at constant temperature until precipitation occurred. Although this doesn't measure the ester content directly, it puts practical bounds on the useful lifetime of these solutions during heating. Fig. 7 shows the Arrhenius plot of the reaction times, including the linear regression to the observed data. The slope of this line is 8126, yielding an activation energy of 67.6 kJ/mole or 0.70 eV. Since the process includes both the time to form the ester and the need to nucleate

TABLE II Stable reaction times for various TIP-HOAc mixing ratios. All data were gathered at 73 °C

TIP:HOAc (mixing ratio)	Reaction time (min)
1 : 2	141 ± 9
1 : 4	133 ± 3
1 : 6	70 ± 3

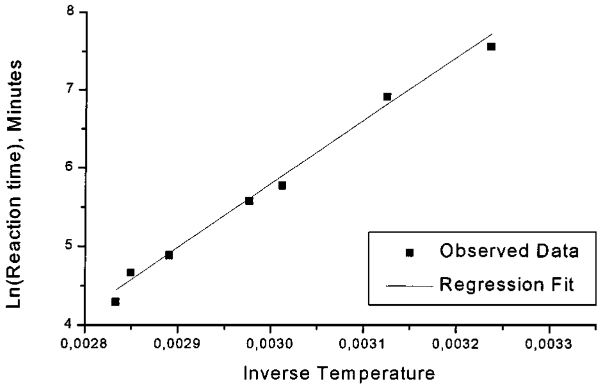

Figure 7 Influence of temperature on the time for the reaction to progress far enough to cause precipitation.

and grow the resultant precipitate, it is not possible to associate this energy with any specific reaction step.

The effect of TIP-HOAc ratio on the time to precipitate has also been tested. Table II gives these results, showing that when the acetic acid concentration is increased beyond the 1 : 4 level, the reaction progress much faster, while a reduction in acetic acid shows relatively little effect. These results will be discussed further in the next section.

5. Discussion

The reaction times for different TIP : HOAc mixing ratios could give information about the reaction which is responsible for the ester production in these solutions. As stated above, several different reactions are possible (see Reactions (2) through (5) above). Each reaction's rate will depend in a different way on the solution species concentrations. Although these contributions can be estimated to a qualitative extent, none of the reactions above can explain the entire span of data.

The general behavior is for faster reaction with higher HOAc content. This argues in favor of either reaction 2 or reaction 4, while Reactions 3 and 5 should be only weakly influenced (and in the opposite direction since the HOAc addition will effectively dilute the other solution species). The occurrence of reaction 2 is also probably not favored because a simple mixture of isopropanol and acetic acid without any TIP was found to generate much smaller quantities of ester during heating under the same conditions. It is also possible that the TIP and various HOAc additions perform some catalytic function in reaction 2, although the present data cannot be used to propose a model for these effects.

As noted earlier, the production of ester occurs along with the condensation of the titanium oligomers. So, as the esterification reaction advances, the average size of the titanium oxo-acetate molecules will increase. Using Equation 6 above and the data presented in Fig. 6, it can be seen that solutions reach reaction extents of around $R = 0.8$ before precipitation occurs. By examining Equation 6 it will be seen that on average there will be nearly 0.8 oxo bridges per titanium at this point.

For comparison, it should be noted that a dimer molecule would have $R = 0.500$, while both singly and doubly oxolated trimers could exist, having R's equal to 0.333 and 0.667, respectively. Linear oxo-bonded titanium chains having length N would have $R = (N - 1)/N$, giving values near 1.0 with very long chains. Using this identity, the R value of 0.8 would suggest an average chain length around 5 (with a wide distribution of both smaller and larger lengths). Finally, the hexamer species, which is thought to be the main precipitate, has $R = 0.667$.

Just before precipitation, the solution must have a large hexamer concentration (with $R = 0.667$), so having the solution average around 0.8 suggests that plentiful longer chains will also be present late in the reaction. In fact, FTIR analysis of the reaction product after precipitation (90 min at 80 °C) gave $R = 0.92$, supporting a gradual approach to longer linear titanium oxo-polymers. In addition, the solutions gathered at longer reaction times (30 min and beyond) were significantly more viscous than the starting mixture. Although this effect was not quantified, it provides qualitative support for the presence of appreciable concentrations of long chain polymers.

It has been suggested that two trimer units may react together to form the hexamer units [22]. However, it is also possible that linear chains can wrap around so that they react end-to-end. This possibility is supported by the average chain length in solution deduced above. Since the solutions certainly contain a spectrum of precursor sizes, it is not possible to distinguish which mechanism is operative in forming the final insoluble oxo-acetate molecules.

The linearity of the temperature dependence (Arrhenius plot given in Fig. 7), suggests that a single step of the total process is rate limiting and has an activation energy near 0.7 eV. However, there are three steps that are required in order to reach the observable precipitation point. First, ester formation must occur to beyond the solubility limit to reach the critical supersaturation concentration. Second, nucleation of precipitate particles must occur. And finally, these particles must grow up to a size that is visible to the naked eye. Since these three steps are sequential, it is not possible to directly associate the activation energy with any one of these steps. These effects may also play a role in the differences found for the different TIP : HOAc mixing ratios tested.

It is instructive to compare R values for two distinct temperatures. The present study has measured R values at 80 °C, while limited data at room temperature are already available in the literature [21]. If these data are normalized according to their respective anticipated times to precipitation using the regression fit, then the ester quantities formed at the two temperatures can be compared. The data, shown in Fig. 8, are in surprisingly close agreement. This may suggest that it is the ester formation itself which is rate limiting.

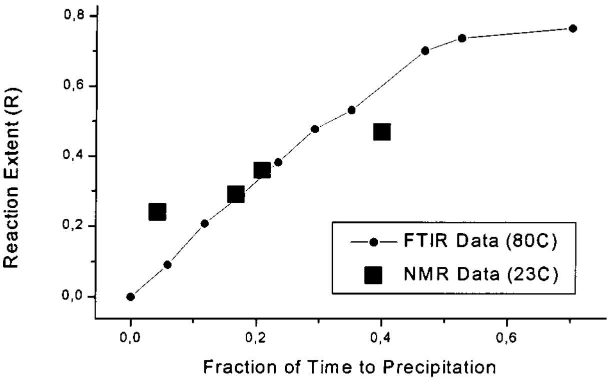

Figure 8 Level of condensation between titanium precursors deduced from the evolution of ester concentration in solution. Comparison of data at different temperatures. NMR data are from reference [21].

With the explanation of the reaction pathway presented above, the changes in the FTIR spectra during reaction can be further interpreted. Fig. 5 above showed these FTIR spectra with annotations indicating general peak position and intensity trends with increasing reaction times. In addition to the growth of the peaks associated with ester formation, there were two broad peaks arising from bidentate acetate groups (around 1425 and 1575 cm^{-1}). It can be seen that both of these peaks must be convolutions of two or more basic signals, and therefore indicate different coordination or bonding modes of the acetate groups. It should be noted that the symmetric stretch vibration of the acetate group (near 1425 cm^{-1}) is also convoluted with the CH_3 deformation mode at 1375 cm^{-1}. However, since this part of the acetate and isopropyl molecules is relatively far from the bonding site there is no appreciable change in intensity or position.

With increasing reaction time, the broad peak around 1425 cm^{-1} increases slightly in intensity, while the peak centered at 1575 cm^{-1} has shifted gradually toward smaller wavenumbers, ultimately reaching 1550 cm^{-1} or less. These gradual changes in the two peaks are evidence of changing contributions from the different types of acetate groups that occur in the solution.

Earlier work has been focused at determining the acetate coordination mode by measuring the separation between these two peaks [30, 32, 33]. In general, wider separations (around 200 cm^{-1} and higher) indicate unidentate bonding of the acetate group. And, rather close spacing (100 cm^{-1} and below) indicate a chelating bidenate mode of attachment. Separations that are between these bounds usually indicate bidenate bonding, but are not diagnostic of whether the two oxygens chelate a single metal, or bridge two nearby metal atoms. Thus, the separations found above (150 cm^{-1} at the start and 125 cm^{-1} near the end) are not able to identify the specific coordination of the acetate ions in the present reactions.

The reaction scheme proposed above would indicate that early reaction times would be dominated by the as-modified species and later times would have larger contributions from the oxo-bridged chain structures. Although the di-acetate modified TIP structure has not been fully characterized in solution, it is known that (contrary to other alkoxides of titanium) the starting TIP is monomeric [34, 35]. Thus, with the substitution of two chelating acetate groups, the titanium could reach a six-fold oxygen coordination mode and would probably stay monomeric in solution. Therefore, the peak positions at early times are most likely indicative of a preponderance of chelating bidentate acetate groups.

Earlier crystal structure examinations of precipitates from TIP-HOAc reaction products gave hexamer structures as shown above [25–27]. For these molecules, all acetate groups are actually bidentate and bridge between two titanium octahedra. From this data it is not possible to determine whether other oxo bonded titanium oligomers also have bridging acetate groups. However, the closer proximity of the titanium atoms to each other could possibly allow the bridging mode. And, since a certain solution concentration of the hexamers must be reached before precipitation can occur, we can suppose that they lead to a significant contribution to the FTIR signal. For these reasons, the late-time spectrum is likely to contain a large fraction of bridging bidentate acetate groups.

If the association found here is true, then the chelating acetate groups actually have a slightly wider peak separation than the bridging acetate groups. This is somewhat unusual when considering the trends presented in the literature, but both separation values are well within the commonly observed ranges. Further FTIR studies (coupled with other structure determination methods) will be required to verify the correlations found in the present work.

6. Conclusions

FTIR measurements have been performed on various mixtures of TIP and acetic acid. These FTIR spectra have been taken at all stages of reaction, from the earliest times until the reactions resulted in precipitation. Although no specific reaction mechanism was deduced by the present experiments, bounds were established for their stable heating without precipitation. In addition, new information about FTIR peaks and their association with bonding environment of the acetate groups has been inferred.

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