Preparation of Carboxylato-Coordinated Titanium Alkoxides from Carboxylic Anhydrides: Alkoxido Group Transfer from Metal Atom to Carbonyl Group

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Reaction of titanium(IV) isopropoxide, Ti(OiPr)4, with an equivolamount of phthalic anhydride resulted in the transfer of an isopropoxido group from the metal atom to one carbonyl group of the anhydride and coordination of the thus formed monoester to the titanium atom. One monoester ligand in Ti2(OiPr)6(μ2-OOC-C6H4-COOOiPr)(η1-OOC-C4H4- COOiPr)(η1-OOC-C4H4-COOOiPr) is bridging and the other is η1-coordinated. When the reaction is performed in the presence of 1 mol-equiv. of acetic acid, the oxido cluster Ti6(μ2-OiPr)(μ2-OOC-C6H4-COOOiPr) was instead obtained. The μ3-oxo groups in the latter compound are due to esterification of acetic acid by the cleaved isopropyl alcohol.

Introduction

Carboxylic acids are frequently used to moderate the reactivity of metal alkoxides, M(OR)n, for sol-gel processing. This is not a straightforward reaction, however, because oxido clusters of the type M2Ox(OH/OR)(OOCR)n are often obtained instead of the substitution products M(OR)m–n (OOCR)n.[1,2] The case of Ti(OR)4 has been particularly well investigated. Spectroscopic analysis of the reaction of Ti(OBu)4 with an equimolar quantity of acetic acid suggested that [Ti(OR)2(OOCR)n]0 (n = 2 or 3) was formed and that the acetate ligands were bridged.[3] A corresponding structure was found for crystalline Ti2(OCH2CMe3)6(OOC-CMe3)2, with bulky alkoxide and carboxylato ligands.[4] The compound Ti2(OiPr)6(μ2-OOC-CMe3)(η1-OOC-CMe3)- (η1-OOC-CMe3)- (η1-OOC-CMe3)- (iPrOH) possibly represents an intermediate state in the coordination of Ti(OR)4 by the second carboxylato ligand. One carboxylato ligand is only monodentate, and the vacant coordination site at the other titanium atom is occupied by an isopropyl alcohol molecule hydrogen-bonded to the dangling oxygen atom of the monodentate carboxylyato ligand.[4] In most reactions of Ti(OR)4 with carboxylic acids, however, carboxylato-coordinated oxido/alkoxido clusters Ti2Ox(OH)(OOCR)n have been obtained.[2]

The most probable sequence of reactions leading to the formation of such clusters is that one or more alkoxido ligands are replaced by carboxylato ligands in the first step (see above), followed by esterification of the liberated alcohol. The thus produced water could be the source of oxido or hydroxido ligands in the clusters. This possibility is also supported by a few cases, where compounds with coordinated water molecules were isolated from such reactions, such as Zr2O4(OH)d(isobutyrate)2(H2O)[5] or a series of hydrated yttrium carboxylates.[6] The carboxylic acids employed in the reactions with metal alkoxides thus have a dual role: as a source for the bidentate ligands to cap the core of the formed clusters and to provide water through esterification reactions.

In the work reported in this article, we attempted to decouple these two functions. To this end, we treated a carboxylic anhydride with Ti(OiPr)4. We chose the anhydride of a dicarboxylic acid (phthalic anhydride), because the groups formed during the reaction are linked with each other and thus easier to identify. The results reported in this article provide new insight into reactions of metal alkoxides with carboxylic acids.

Results and Discussion

Reaction of Ti(OiPr)4 with an equivolamount of phthalic anhydride in isopropyl alcohol resulted in the quantitative formation of crystalline Ti2(OiPr)6(μ2-OOC-C6H4-COOOiPr)(η1-OOC-C6H4-COOOiPr)(η1-OOC-C6H4-COOOiPr)(iPrOH) (1)[Equation (1)]. The molecular structure of 1 is analogous to that of Ti2(OiPr)6(μ2-OOC-CMe3)(η1-OOC-CMe3)(η1-OOC-CMe3)(η1-OOC-CMe3)(iPrOH) mentioned before.[4] The two titanium atoms in the asymmetric dimer are bridged by two OiPr ligands and one phthalate monooester ligand (Figure 1). The octahedral cooordination of Ti(1) is completed by coordination of an η1-phthalate monooester and two terminal OiPr ligands, and that of Ti(2) by three terminal OiPr ligands.

Because of the bridging carboxylato ligand, the [TiO3] coordination octahedra are slightly tilted towards this ligand. The carbonyl oxygen O(13) of the η1-phthalic ester and that of the adjacent OiPr ligand O(5) at the neighboring titanium atom are clearly connected through a hy-
drogen bond [O(5)···O(13) 260.3(2) pm]. The hydrogen atom was located in difference Fourier maps, and was close to O(5) of the O\textsubscript{iPr} ligand [O(5)–H(5D) 81(3) pm] with an O(5)–H(5D)–O(13) angle of 175(3)°, corresponding to a co-ordinated iPrOH molecule. This can also be concluded from the Ti(2)–O(5) distance [207.20(12) pm], which is much longer than that of the Ti–O distances of the other terminal O\textsubscript{iPr} ligands (177.8–181.9 pm). Furthermore, the C(33)–O(13) distance is 124.2(2) pm, which is only slightly longer than that of the ester CO group in the bridging ligand [C(29)–O11) 120.4(2) pm]. The stabilization of an η\textsuperscript{1}-carboxylato ligand by means of a hydrogen bond to the oxygen atom of an adjacent ligand was also observed in Zr\textsubscript{6}O\textsubscript{4}(OH)\textsubscript{4}(isobutyrate)\textsubscript{12}(HX) (HX = H\textsubscript{2}O or BuOH).

Solution NMR spectroscopic data are in line with the solid-state structure, but a clear assignment of individual signals (especially in the phenyl and O\textsubscript{iPr} areas) is not possible due to the different groups with similar chemical shifts.

Although the general structure type represented by 1 has been observed before (see above), the formation of I is remarkable. Substitution of metal alkoxides is usually performed by reaction with protic compounds (HY) during which the proton of HY is transferred to an OR group with subsequent elimination of ROH (Scheme 1; X = H, for Y = OOCR\textsuperscript{−}). In a similar manner, an alkoxido group could be transferred to the R’C(O) moiety of the anhydride with concomitant formation of an ester (Scheme 1; X = R’CO). The resulting carboxylato ligand is coordinated to the titanium atom. If a cyclic anhydride is used, as in the case of phthalic anhydride, the ester and carboxylate groups remain of course attached to each other.

![Figure 1](image_url)

**Figure 1.** Molecular structure of Ti\textsubscript{2}(O\textsubscript{iPr})\textsubscript{6}(μ\textsubscript{2}-OOC-C\textsubscript{6}H\textsubscript{4}-COO\textsubscript{iPr})(η\textsuperscript{1}-OOC-C\textsubscript{6}H\textsubscript{4}-COO\textsubscript{iPr})(iPrOH) (1). Selected distances [pm] and angles [°]: Ti(1)–Ti(2) 322.74(6), Ti(1)–O(1) 177.82(13), Ti(1)–O(2) 181.07(13), Ti(1)–O(6) 205.37(12), Ti(1)–O(7) 204.92(12), Ti(1)–O(8) 210.41(11), Ti(1)–O(9) 198.09(12), Ti(2)–O(3) 181.92(12), Ti(2)–O(4) 177.34(12), Ti(2)–O(5) 207.20(12), Ti(2)–O(6) 202.85(11), Ti(2)–O(7) 202.86(12), Ti(2)–O(9) 206.17(11), Ti(1)–O(6)–Ti(2) 104.48(5), Ti(1)–O(7)–Ti(2) 104.64(5), O(7)–Ti(1)–O(6) 72.82(5), O(6)–Ti(1)–O(8) 85.80(5), O(7)–Ti(1)–O(8) 84.57(5), O(1)–Ti(1)–O(7) 163.25(5), O(12)–Ti(1)–O(8) 175.49(5), O(4)–Ti(2)–O(6) 168.56(5), O(3)–Ti(2)–O(7) 166.26(5), O(6)–Ti(2)–O(7) 73.78(5), O(9)–Ti(2)–O(5) 171.52(5).

No protic compounds are involved in the reaction with phthalic anhydride. No water or hydroxido groups can therefore be formed, and hence no oxido/hydroxido clusters. To gain further insight into the role of carboxylic acids in reactions with metal alkoxides, we modified the above reaction in a way that an equimolar amount of acetic acid was added to the isopropyl alcohol solution of Ti(O\textsubscript{iPr})\textsubscript{4} and phthalic anhydride. This allowed a competition between a carboxylic acid and a carboxylic anhydride as potential sources for carboxylato ligands.

After a long reaction period, crystals of the centrosymmetric cluster Ti\textsubscript{6}O\textsubscript{6}(O\textsubscript{iPr})\textsubscript{6}(OOC-C\textsubscript{6}H\textsubscript{4}-COO\textsubscript{iPr})\textsubscript{6} (2) were isolated [Equation (2)]. The IR spectrum of the supernatant solution showed a broad peak at 1723 cm\textsuperscript{−1} indicating ester formation. For comparison: the ν\textsubscript{CO} band of isopropyl acetae is at 1735 cm\textsuperscript{−1} and that of acetic acid at 1710 cm\textsuperscript{−1}. The cluster core of 2 can be described as a Ti\textsubscript{6} octahedron in which six of the eight triangular faces are capped by μ\textsuperscript{3}-oxygen atoms or as a slightly distorted hexagonal prism with alternating titanium and oxygen atoms. The six phthalate isopropyl ester ligands bridge the six four-membered Ti\textsubscript{2}O\textsubscript{2} rings of the hexagonal prism. Each titanium atom is octahedrally coordinated by two phthalate ester ligands, one terminal O\textsubscript{iPr} ligand and three μ\textsuperscript{3}-oxygen atoms. The terminal OR ligands are oriented perpendicular to the slightly puckered Ti\textsubscript{3}O\textsubscript{3} rings. This structural motif was already found in other Ti\textsubscript{6}O\textsubscript{6} clusters obtained by reaction of titanium alkoxides with various carboxylic acids\textsuperscript{[7]} or oximes.\textsuperscript{[8]}

The bond lengths and angles observed in 2 are in the same range as in the reference compounds.

Compound 2 only contains phthalate monoester ligands but no acetato ligand (Figure 2). This is remarkable, because two potential sources for carboxylato ligands were
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Figure 2. Molecular structure of Ti$_6$O$_6$(OiPr)$_6$(OOC-C$_6$H$_4$COOiPr)$_6$ (2). Selected distances [pm] and angles [°]: Ti(1)–O(1) 190.3(4), Ti(1)–O(2) 187.0(4), Ti(1)–O(3) 213.7(4), Ti(1)–O(4) 176.0(4), Ti(1)–O(7) 205.6(5), Ti(1)–O(11) 206.4(4), Ti(2)–O(1) 215.5(4), Ti(2)–O(2) 192.1(4), Ti(2)–O(3) 187.3(4), Ti(2)–O(5) 174.7(4), Ti(2)–O(8) 205.0(5), Ti(2)–O(15) 207.4(4), Ti(3)–O(1) 188.5(4), Ti(3)–O(2) 216.8(4), Ti(3)–O(3) 192.5(4), Ti(3)–O(6) 176.6(4), Ti(3)–O(12) 208.2(4), O(1)–Ti(1)–O(2) 103.0(2), O(1)–Ti(1)–O(3) 77.5(2), O(1)–Ti(1)–O(4) 99.7(2), O(1)–Ti(1)–O(7) 86.0(2), O(1)–Ti(1)–O(11) 158.6(2), O(1)–Ti(2)–O(2) 78.0(2), O(1)–Ti(2)–O(3) 77.7(2), O(1)–Ti(2)–O(5) 177.8(2), O(1)–Ti(2)–O(8) 88.5(2), O(1)–Ti(2)–O(15) 88.1(2), O(1)–Ti(3)–O(2) 78.4(2), O(1)–Ti(3)–O(3) 101.4(2), O(1)–Ti(3)–O(6) 105.3(2), O(1)–Ti(3)–O(12) 157.9(2), O(1)–Ti(3)–O(16) 86.5(2).

Present in the reaction mixture (in a 1:1 ratio). It is rather obvious that the phthalate monoester ligands were formed by the same reaction as in 1. On the other hand, the μ$_3$-oxygen atoms in 2 must be due to esterification of acetic acid. Since formation of 2 was much slower than that of 1, it can be assumed that reaction of the anhydride (giving the phthalate monoester ligands) is faster than that of acetic acid (resulting in partial hydrolysis). Although we could not identify other species, which may be present in the reaction solution, it appears that the role of acetic acid was to provide the water for hydrolysis of part of the alkoxide groups (through formation of isopropyl acetate), while phthalic anhydride served to replace part of the alkoxide groups.

Conclusions

The results reported in this paper strongly support the notion that the first step of the reaction of Ti(OR)$_4$ with carboxylic acids is the formation of carboxylato-coordinated titanium alkoxides Ti(OR)$_{n-x}$(OOCR)$_x$ ($x = 1$ or 2). In the case studied here, i.e. the reaction of a carboxylic anhydride, the carboxylato ligand was formed by a route that excludes the formation of water or OH species and thus the formation of oxido/hydroxido clusters. The carboxylato ligand, which eventually was coordinated to the titanium atom, was generated by OR group transfer from the metal atom to the other CO group of the anhydride. Formation of 1 was a surprisingly fast and quantitative process.

When the system was modified in a way that slow internal water production was possible (with otherwise the same reaction conditions), the oxido/alkoxido cluster 2 was obtained instead. The added acetic acid is the only possible source of the oxido groups. If one assumes that formation of 1 is the first step in the formation of 2 (because formation of 1 is very fast), two OiPr ligands must be subsequently be replaced by one oxido groups, while the Ti/OOCR ratio is retained. The formal equation 2 O$i$PrO– + CH$_3$COOH $\rightarrow$ CH$_3$COO$i$Pr + $i$PrOH + O$^2$ shows that 1 mol-equiv. of acetic acid per titanium is sufficient to explain the outcome of the overall reaction.

Experimental Section

General: All compounds were handled under argon by using standard Schlenk techniques. Isopropyl alcohol was dried by distilling twice from sodium, acetic acid was freshly distilled from P$_2$O$_5$ prior to use, Ti(OiPr)$_4$ and phthalic anhydride were used as received from Aldrich.

Ti$_2$(OiPr)$_6$(μ$_2$-OOC-C$_6$H$_4$COOiPr)(η$_1$-OOC-C$_6$H$_4$COOiPr)-(OiPrOH) (1): Ti(OiPr)$_4$ (1.08 g, 3.8 mmol) was added to a suspension of phthalic anhydride (560 mg, 3.8 mmol) in isopropyl alcohol (291 μL, 3.8 mmol). The mixture was heated until a clear solution was obtained. Crystals were obtained at room temperature within 24 h. Yield 1.86 g (100%). 1H NMR (CD$_2$Cl$_2$, 300 MHz): δ = 1.29 (d, $J = 6.1$ Hz, 42 H, CH$_3$), 1.39 (d, $J = 6.0$ Hz, 12 H, CH$i$-iso- propyl ester), 4.60–5.20 (7 H, CH, O$i$Pr), 5.25 (m, 2 H, CH$i$-iso- propyl ester), 7.3–7.7 (m, 6 H, CH, Ph), 8.12 (2 H, CH-C-COO$i$Pr)
Table 1. Crystallographic data for 1 and 2.

|   | 1                          | 2                          |
|---|----------------------------|----------------------------|
| Empirical formula | C$_{64}$H$_{108}$O$_{36}$Ti$_6$ | C$_{64}$H$_{71}$O$_{15}$Ti$_2$ |
| $M_r$ | 1981.1                     | 1923.8                     |
| Space group | triclinic                   | triclinic                   |
| $a$ [pm] | 1148.9(2)                  | 1209.95(7)                 |
| $b$ [pm] | 1177.70(18)                | 1368.20(8)                 |
| $c$ [pm] | 1944.0(3)                  | 1458.24(7)                 |
| $\alpha$ [°] | 103.090(6)                 | 85.570(4)                  |
| $\beta$ [°] | 97.570(9)                  | 66.340(4)                  |
| $\gamma$ [°] | 99.780(8)                  | 78.120(4)                  |
| $V$ [pm$^3$] | 2484.7(7)                 | 2308.62(6)                 |
| Z | 2                          | 1                          |
| $D_r$ [Mg m$^{-3}$] | 1.236                     | 1.425                     |
| $\mu$ [mm$^{-1}$] | 0.382                     | 0.579                     |
| Crystal size [mm] | 0.4 x 0.32 x 0.3          | 0.2 x 0.18 x 0.14          |
| No. measured, independent, observed refl. [I > 2σ (I)] | 72908, 14419, 11404 | 11300, 6535, 3965 |
| $R_{int}$ | 0.0356                    | 0.0476                    |
| $\theta_{max}$ [°] | 30.01                    | 23.25                    |
| $R (I^2 > 2σ(F))$, wR (F) | 0.0439, 0.1206, 1.028 | 0.0670, 0.2028, 1.027 |
| No. reflections/parameters | 14419/635                | 6535/580                  |
| Weighting scheme | $w = 1/[σ(^2(F)) + (0.0529P)^2 + 1.8451P]^d$ | $w = 1/[σ(^2(F)) + (0.1108P)^2 + 1.4297P]^d$ |
| $\delta_{max}$, $\delta_{min}$ [e Å$^{-3}$] | 1.312, –0.693 | 0.946, –0.602 |

[a] $P = (F_o^2 + 2F_c^2)/3$.

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