Fourier transform infrared spectra of three titanium tetrachloride-ethyl benzoate complexes. Assignment based on five isotopic homologues and extension of the ethyl benzoate force field

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Abstract—FTIR spectra (200-1750 cm⁻¹) are given for $(TiCl_4EB)_2$, $(TiCl_4)_2EB$ and $TiCl_4EB_2$, where EB is ethyl benzoate. A full assignment is given for $(TiCl_4EB)_2$ based on extension of an ethyl benzoate force field and four isotopically labelled complexes with ¹⁸O-carbonyl-EB, d_5 -EB, Ed_5 -B and d_5 -Ed, -B. There is no evidence for bidentate complexation or complexation through the ether oxygen in any of the complexes. A strong coupling between the α -C-O stretching vibration and the ethyl group deformations can make simplified interpretations of differences between spectra misleading.

INTRODUCTION

Most of the interest in studying vibrational spectra of ethyl benzoate and its titanium tetrachloride complexes is linked to the use of the ester in Ziegler-Natta catalysts, especially the magnesium chloride supported high activity catalysts for isotactic polymerization of propene [1-3]. However, the mechanism for the polymerization with these catalysts is far from understood, which to a large extent is due to an inferior understanding of the chemistry of the components involved.

The basic constituent of these catalysts is titanium tetrachloride, which constitutes the active centers of the catalyst. Anhydrous magnesium chloride makes the support, and an organic ester (called internal donor) is used to reduce crystallite size and increase surface area [4-6], to increase titanium content in the catalyst [7], and to improve overall activity [8]. The catalyst (sometimes called a procatalyst) is activated with an aluminum alkyl compound, and is moderated with an external donor, which may be an organic ester [9-11] or, in more recent studies, alkoxy-silanes [12-14]. The effect of the moderator is to improve the overall stereoregularity (isotacticity) of the polymer.

Ethyl benzoate is one of the most used organic esters for the magnesium chloride supported catalysts, both as internal donor [15-27] and as external donor [14, 27-33], also for catalysts for polymerization of other olefins like ethene [34], styrene [35, 36], for α -olefins in general [37] and in copolymerizations [38, 39]. Although the functions of the ester as promotor when used as internal donor and as moderator when used as external donor are well established, the actual mechanisms for these effects are still obscure.

FTIR spectroscopy has proved to be an important tool in the elucidation of these mechanisms. Through several studies, it has been proved that the ester mainly coordinates to magnesium chloride in the catalyst [4, 26, 27, 40–45]. However, a small amount of the ester is, at least for some catalysts, coordinated to titanium [26] or in ternary complexes [26, 46], and this coordination may be crucial for the formation of active catalytic centers. It is known that only a fraction of the titanium complexes in the catalyst makes active centers [47–52]. Compounds which appear in minor quantities in the catalyst may therefore be related to the active centers.

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However, both in these studies and in several studies of related complexes, the complex nature of the spectra has restricted the interpretation to the observation of changes in the C=O stretching frequency [53-59]. Some authors have investigated changes in the α -C-O stretching band [27, 56-61] but as will be shown in this paper, a correct interpretation is very difficult without a deeper understanding of the spectrum.

The aim of the present work is therefore to supply the information needed to facilitate deeper analyses of the spectra, and thereby utilize more of the large amount of hidden information. The present work will probably also be useful for the interpretation of vibrational spectra of the related diester complexes (i.e. phthalates and terephthalates) which have been shown by X-ray crystallography to have structures similar to those of the EB complexes [62–64], and which seem to be even more promising as internal donors in the catalysts [12–14].

The present work was performed as a part of a research project which has included both kinetic and structural studies of the catalyst [26]. A detailed study of the vibrational spectra of ethyl benzoate [65] employing force field calculations and isotopic labelled compounds [66–67] has already been reported, together with the detection of a new crystalline phase of the ester [68]. We now report a detailed analysis of the titanium tetrachloride complexes. This study has led to the detection of a new titanium tetrachloride complex [69], and a surface complex on the catalyst which seems to be linked to catalyst activity [26]. In the near future we will report a more detailed vibrational analysis of the ester, including nine isotopic congeners [70].

EXPERIMENTAL

Parent ethyl benzoate (99%, Fluka, Switzerland) and titanium tetrachloride (99%, Fluka, Switzerland) were distilled prior to use. There was no yellowish tint in the $TiCl_4$.

The labelled esters were made from $H_2^{18}O$ (90% isotopic purity, Stohler, U.S.A.), d_6 -ethanol (99%, anhydrous, Stohler) and d_6 -benzene (99%, Stohler) by standard techniques. The sample of the fully deuterated ester was too small to allow any distillation, and had a residual content of d_5 -benzoic acid estimated to 2–5%. A small content of d_5 -benzoic acid was also seen in the IR spectrum of ethyl d_5 -benzoate, probably well beyond 1%. These residual acid contents are probably responsible for the oxychloride impurities found in the complexes made from the d_5 -benzoate esters. Details of the syntheses are given elsewhere [71].

The neat ethyl benzoate samples were prepared by deposition of gaseous ethyl benzoate on a liquid nitrogen cooled CsI window in a vacuum chamber (Fig. 1). The ester liquid was contained in a Schlenk flask, and the ester vapor was led through a lead seated needle valve and through a thin canula ($\phi = 0.5$ mm). The outlet of the canula was *ca* 2 cm from the CsI window. The ester was heated to 30-45 °C to obtain a reasonable deposition rate, and deposition times of 30-60 min provided the best samples.

For preparation of the titanium tetrachloride complexes, the ester and titanium tetrachloride were deposited simultaneously from each of the two identical Schlenk flasks, and the vapours led through two separate needle valves and canulas. The TiCl₄ flask was kept at ambient temperature $(ca 25 \,^{\circ}\text{C})$ during this procedure. The outlets of the two canulas were less than 3 mm apart, and the components may have reacted in gas phase before reaching the cold CsI window. TiCl₄ was added in excess, but there was no independent measurement of the amounts of the two components, or of the stoichiometry of the final sample.

Prior to sample preparation the vacuum of the cell was better than 10^{-2} Pa. The vacuum was provided by a turbo molecular pump, and was continuously monitored during the depositions. There was no independent measurement of the temperature at the CsI window. During the codeposition of ester and TiCl₄, an increased evaporization of nitrogen from the Dewar was observed, indicating liberation of heat.

The FTIR spectra were recorded on an evacuable Bruker IFS 113v FTIR instrument. The instrument was equipped with a DTGS detector and a 3.5 μ m Mylar film beamsplitter for the 200–700 cm⁻¹ region, and an MCT detector and a Ge/KBr beam-splitter for the 500–4000 cm⁻¹ region. All spectra were recorded with a Globar source, and using a 4 cm⁻¹ nominal resolution (half height width). Trapezoidal apodization was employed. Numerical extension of the interferogram ensured peak position accuracy of ± 1 cm⁻¹ for all spectra.



Fig. 1. Experimental set up for preparation of samples of ethyl benzoate and TiCl₄-EB complexes at -196 °C under vacuum. Above: side view. Below: top view, simplified. 1, Liquid nitrogen Dewar; 2, Cu tube; 3, O-ring, allowing twist of the upper part of the cell; 4, CsI windows; 5-7, not used in this work; 8, canula; 9, needle valve; 10, metal-glass junction, 11, Schlenk flasks for liquid EB and TiCl₄.



Fig. 2. Schematic structure of (a) (TiCl₄EB)₂, (b) TiCl₄EB₂ and (c) (TiCl₄)₂EB. The structures (a) and (b) are determined from single crystal X-ray diffraction [26, 72], whereas (c) is postulated from vibrational spectra [69].



Fig. 3. FTIR spectra at -196 °C for crystalline (xl) and amorphous (am) (TiCl₄EB)₂, TiCl₄(EB)₂ and (TiCl₄)₂EB in the frequency region 600-1750 cm⁻¹. "X" denotes a titanium oxychloride impurity.

RESULTS AND DISCUSSION

The (TiCl₄EB)₂ *complex*

Crystalline $(TiCl_4EB)_2$ was formed when $TiCl_4$ and EB were codeposited at relatively high deposition rates, with excess $TiCl_4$. The reaction heat was seemingly enough to drive off excess $TiCl_4$ from the sample and allow the complex to crystallize.



Fig. 4. FTIR spectra at -196 °C for crystalline (TiCl₄EB)₂ with parent, ¹⁸O-carbonyl and d_5 -ethyl ester. "X" denotes traces of parent ester in the ¹⁸O-labelled compound. The broad feature at *ca* 800 cm⁻¹ for the ¹⁸O labelled complex is due to titanium oxychloride impurities. The shoulder at 1406 cm⁻¹ in the spectrum of the deuterated complex is due to traces of (TiCl₄)₂ d_5 -EB [69].

The structure of this complex (Fig. 2a) has been determined by GUOLIN *et al.* [72], and in details by RYTTER *et al.* [26], who also have provided FTIR spectra of a Nujol suspension of the crystals [73]. The uppermost spectra in Figs 3 and 4 identify the sample as $(TiCl_4EB)_2$. Figure 3 also gives the IR spectrum of a probably amorphous phase of the same complex, the spectrum differs by broader bandwidths and some minor frequency shift. The latter sample was made when using a reduced deposition rate.

In Table 1 the vibrational frequencies of the complex $(TiCl_4EB)_2$ at -196 °C is compared with the vibrational frequencies of the neat ester at the same temperature. The assignment is based on a force field calculation for ethyl benzoate which is described in detail elsewhere [65, 71].

Most of the assignments are trivial when compared with the neat ester and the isotopic shifts. However, some points deserve to be mentioned.

The most prominent feature of the spectrum is the two strong bands at $1560-1600 \text{ cm}^{-1}$. Substitution with ¹⁸O in the carbonyl group reduces the lower of the two frequencies *ca* 16 cm^{-1} . This band is therefore assigned to the C=O stretching

EB	(TiCl _← EB) ₂	Simplified assignment [†]	Symmetry‡	
1713 (-26) vs 1566 (-16)		Carbonyl stretching§	A'	
1615 w	1617 sh	Combination 999+615		
	1543 (-20) sh	1		
	1510 (-10) w	¶		
1603 m	1605 sh	Phenyl	Α'	
1585 m	1594 (-3) vs	Phenyl	Α'	
1492 w	1494 w	Phenyl	A'	
1477 w	1468 s	Methylene scissoring	A'	
1466 w	1467 (?) sh	Methyl deformation	A"	
1451 m	1452 (-2) m	Phenyl	Α'	
1444 sh	1445 sh	Methyl deformation	Α'	
1393 m	1417 (-3) s	Methylene wag	Α'	
1367 m	1383 s	Methyl umbrella	Α'	
	1349 sh	1		
	1322 w	Î		
1314 s	1310 s	Phenyl	Α'	
1280 vs	1333 vs	α -C-O stretching	Α'	
	1279 w	Phenyl	Α'	
1264 sh	1252 vw	Methylene twist	A"	
1176 m	1184 m	Phenyl	Α'	
1159 m	1164 w	Phenyl	Α'	
	1152 w	Combination 711 + 443 (?)		
1125 (-2) s	1170 (-7) w	Skeletal stretch	Α'	
1110 s	1117 w	Skeletal stretch	A'	
1100 sh	1101 w	Methyl wag	A"	
1071 m	1075 w	Phenyl	A'	
1028 m	1025 m	Phenyl	Α'	
1010 w	1010 m	Ethyl C-C stretching	A'	
999 w	1000 w	Phenyl breath	Α'	
981 vw	981 vw	Phenyl	A "	
940 w	944 vw	Phenyl	A"	
877 w	864 (+2) w	β –C–O stretching	Α'	
	874 (−8) w	Combination 536 + 342 (?)		
853 (-10) w	883 (-15) w	O=C-O scissoring	Α'	
815 w	819 vw	Methylene rock	A"	
809 sh	802 vw	Carbonyl wag	A "	
712 vs	711 s	Phenyl in phase wag	A"	
688 m	680 w	Phenyl deformation	A"	
675 (-2) m	668 (-2) vw	Phenyl deformation	A'	
617 vw	615 vw	Phenyl deformation	A'	
	536 (-8) s	Ti–O stretching	Α'	
	<i>ca 5</i> 00 var	TiO _x Cl _y contaminations		

Table 1. Observed vibrational frequencies for (TiCl₄EB)₂ and EB at -196 °C

Continued on next page

496 (-6) w	?	Skeletal deformation		
	427 s	Ti-Cl stretching		
	413 s	Ti-Cl stretching		
	388 vs	Ti-Cl stretching		
	379 sh	Ti-Cl stretching		
443 vw	?	Phenyl deformation	Α"	
397 vw	?	Phenyl deformation	Α"	
392 (-7) w	342 (?) w	Skeletal deformation	Α'	
331 w	286 (-12) m	Skeletal deformation	Α'	
	280 m	Ti-Cl deformation		
	<i>ca</i> 280 var	TiO _r Cl, contamination		
272 (-3) w	231 (-3) w	Skeletal deformation	Α'	
	203 w	Ti-Cl deformation		

Table 1. Continued

* All frequencies in cm⁻¹, nominal accuracy is $\pm 1 \text{ cm}^{-1}$ for sharp and well defined peaks. Numbers in brackets are observed isotopic shifts with ¹⁸O carbonyl. (?) Denotes uncertain assignment. Intensities are given as visual estimates: vs=very strong, s=strong, m=medium, w=weak, vw=very weak and var=variable intensity.

[†]The assignment is most correct for the neat ester.

 $\ddagger A'$ and A'' symmetry of the vibrations refers to the mirror plane of the ethyl benzoate molecule with C_s symmetry.

§ The frequency of this band may vary from ca 1560 to 1570 cm⁻¹ due to variations in sample thickness a.o.

|| These two bands probably owe a similar amount of their intensity to the C=O stretching vibration.

¶ These bands are left unassigned, but could be due to symmetric vibrations in the nearly centrosymmetric complex.

vibration, but this assignment should not be taken literally. The similarity in band intensities shows that both bands owe a major part of their intensity to the C=O stretching. Furthermore, the dip at 1585 cm^{-1} shows that it is the phenyl mode at this frequency, and not the one at 1603 cm^{-1} , which couples with the carbonyl stretching vibration [74, 75].

Two C=O stretching vibrations should arise from the two C=O groups of the dimer. Although the ester groups are separated by several atoms (Fig. 2a), they should interact to some extent. The complex is centrosymmetric (at least ideally) and only the antisymmetric vibration should be IR active. The two weak bands at 1543 and 1510 cm⁻¹ may be due to the symmetric counterpart of the C=O stretching vibration. This interpretation is supported by the lack of similar bands in the spectrum of TiCl₄EB₂.

The α -C-O stretching vibration is most conveniently assigned to the band at 1333 cm⁻¹ in the complex. However, as will be discussed in connection with the isotopic homologues, this mode couples strongly with several other vibrations, and the assignment is at best a crude simplification.

The triplet at $ca 870 \text{ cm}^{-1}$ seems to merge into one band for the ¹⁸O complex. Only two fundamentals are expected in this frequency range, hence the third band is assigned to a combination band. The individual assignments are open for discussion.

The $TiCl_4EB_2$ complex

The structure of this complex has been determined by GUOLIN *et al.* [72], and in detail by RYTTER *et al.* [26, 73] who also have provided FTIR spectra of a Nujol suspension of the crystals. The structure was found to be an octahedral complex with the two ester ligands *cis* to each other, as shown in Fig. 2b. This structure is also in accordance with a recent NMR study of the complex [76].

This complex appeared only once during the present work, and transformed to the equimolar complex after annealing in vacuum. The IR spectrum shows traces of titanium oxychloride impurities, but this is not expected to influence the spectrum of the complex.

Table 2. Comparison of some selected vibrational frequencies for ethyl benzoate and some of its titanium tetrachloride complexes at -196 °C*

2Ti–EB†‡	Ti–EB	Ti-2EB	EB	
1535 vs	1566 vs	1636 vs	1713 vs	
		1577 vs		
	1605 sh	1602 vs	1603 m	
1598 s	1594 vs		1585 m	
	1494 w	1496 w	1 49 2 w	
1468 s	1468 s	1469 s	1477 w	
1448 s	1452 s	1452 s	1451 m	
1419 vs	1417 s	1411 s	1393 m	
1382 s	1383 s	1376 s	1367 m	
1313 s	1310 s	1310 vs	1314 s	
1337 s	1333 vs	1333 vs	1280 vs	
1277 w	1279 w	1287 w		
1244 vw	1252 vw	1250 vw	1264 sh	
1184 m	1184 m	1182 m	1176 m	
1165 m	1164 w	1163 w	1159 m	
1151 w	1170 w	1152 w	1125 s	
1113 vw	1117 w	1114 w	1110 s	
1098 m	1101 w	1099 w	1100 sh	
1072 w	1075 w	1075 w	1071 m	
1027 m	1025 m	1029 w	1028 m	
994 m	1010 m	1006 m	1010 w	
	1000 w	1000 m	999 w	
942 vw	944 vw	944 vw	940 w	
711 s	711 s	715 s	712 vs	
678 m	680 w	684 w	688 m	
670 vw	668 vw	669 w	675 m	
615 vw	615 vw	616 vw	617 vw	
553 s	536 s	528 s		

* See footnotes for Table 1. All frequencies in cm^{-1} . Intensities are visual estimates.

 $\dagger EB = free ester. 2Ti-EB = (TiCl_4)_2EB.$ Ti-EB = crystalline (TiCl_4EB)_2. Ti-2EB = TiCl_4EB_2.

[‡] This complex has not been prepared for the parent ester. The given frequencies are for the ¹⁸O-carbonyl ester complex, but corrected using the isotopic shifts given for the equimolar complex in Table 1.

The equimolar complex is not seen in the IR spectrum, but the weak feature at ca 1715 cm⁻¹ may be due to a small excess of free EB.

The most important difference compared to the spectrum of the equimolar complex is the strong band at 1636 cm⁻¹ (Table 2). Thus the strong bands in this range end up as a triplet compared to the doublet seen for the equimolar complex. (The C=O stretch at 1636 cm⁻¹ is probably too separated from the phenyl vibration at 1585 cm⁻¹ to couple extensively. If this coupling had appeared we would have seen a quartet.)

The observed triplet requires at least two C=O bonds in the complex, and the two ester ligands must be *cis* to each other. If the bonds had been *trans* to each other, the symmetric stretching of the two bonds would have been of a very low intensity, or would be IR inactive if the complex was perfectly centrosymmetric. The FTIR spectrum therefore verifies the X-ray structure [26, 72, 73].

Other minor differences between the IR spectra of the two complexes may be easily explained in terms of a slightly stronger complexation for the equimolar complex. The differences in the frequency region $700-200 \text{ cm}^{-1}$ (Fig. 5) show that the titanium entities are different, but no further interpretation is attempted.



Fig. 5. FTIR spectra at -196 °C for crystalline (xl) and amorphous (am) (TiCl₄EB)₂, and TiCl₄(EB)₂ in the frequency region 200-700 cm⁻¹. Nominal peak position accuracy is *ca* 1 cm⁻¹ and nominal resolution (half height bandwidth) is *ca* 4 cm⁻¹ for all spectra.

The (TiCl₄)₂EB complex

This complex was formed on three occasions only, every time with isotopically labelled esters. Figure 3 includes the FTIR spectrum of this complex with ¹⁸O labelled ester. The complex appeared when a very high TiCl₄/EB ratio and a slow deposition rate was employed, but we did not succeed in developing a reliable procedure for synthesis of the complex. The strong band at *ca* 500 cm⁻¹ in the IR spectrum of $(TiCl_4)_2EB$ in Fig. 6 is due to excess TiCl₄ in the sample.

The complex is believed to have two octahedral titanium units with three chlorine bridges (Fig. 2c). This configuration is known for other compounds, among others the



Fig. 6. FTIR spectra at -196 °C for $(TiCl_4d_5EB)_2$ and a sample of predominately $(TiCl_4)_2d_5EB$. The latter shows excess free TiCl₄.

Ester	Complex	Shift	Ester	Complex	Shift		Simplified assignment
Ethyl b	enzoate		d ₅ -ethy	l benzoate			
1713 1603	1566 1605	$\begin{pmatrix} -147 \\ +2 \end{pmatrix} = 1$	1714 34 1602	1564 1602	-150	-133	C=O str. Phenyl
1585	1594	+9	1585	1599	+14	100	Phenyl
1492	1494	+2)	1492	1495	+3		Phenyl
1393 1367 1314 1280	1417 1383 1310 1333	+24 +16 + -4 +53	89 1317 1299	1314 1382	-3 +83	+80	CH ₂ wag Umbrella Phenyl α-C-O str.
	536			521			Ti–O str.
Ethyl a	l5-benzoate		d ₅ -ethy	l d ₅ -benzoate	:		
1713 1570 1548	1576 1569 1538	$ \begin{array}{c} -137 \\ -1 \\ -10 \end{array} \right\} \ -1$.48 1570 1549	1586 1569 1538	$ \left. \begin{array}{c} -126 \\ -1 \\ -11 \end{array} \right\} $	-138	C=O str. Phenyl Phenyl
1398 1383 1362 1333 1300 1254	1429 1387 1360 1340 1307 1314	$ \begin{array}{c} +31 \\ +4 \\ -2 \\ +7 \\ +7 \\ +60 \end{array} +1 $	1390 107 1334 1300 1275	1411 1342 1307 1322	+21 +8 +7 +47	+83	CH ₂ wag Phenyl Umbrella Phenyl Phenyl a-C-O str.
	535			510			Ti–O str.

Table 3. Comparison of vibrational frequencies for four hydrogen/deuterium homologues of ethyl benzoate and their equimolar complexes with titanium tetrachloride at -196 °C*

* All frequencies are in cm⁻¹, nominal accuracy $\pm 1 \text{ cm}^{-1}$ for sharp and well defined peaks. For the C=O and phenyl bonds at *ca* 1600 cm⁻¹ there may be variations up to 10 cm⁻¹ for samples of varying thickness. The assignments for the complexes are highly tentative due to a very strong coupling between the vibrations.

ion Ti_2Cl_9 [77]. Furthermore, IR studies indicate that titanium tetrachloride may dimerize at cryogenic temperatures [78]. Hence, the proposed structure, although not proved, should not be regarded as unexpected.

As the ester is *trans* to a bridging ligand, the lower *trans* influence should make the ester more strongly complexed [15]. The stronger complexation is verified by the low C=O stretching frequency and the significantly higher frequencies for the bands at $1300-1420 \text{ cm}^{-1}$ (Fig. 3 and Table 2).

Compared to Fig. 5, Fig. 6 shows important differences in the Ti–Cl vibration frequencies for $(TiCl_4d_5EB)_2$ and $(TiCl_4)_2d_5EB$ especially at *ca* 400 cm⁻¹, but no attempt was made for a more detailed analysis of this part of the spectrum. The Ti–O stretching band can be seen as a shoulder in the lower spectrum, and has a significantly higher frequency than for $(TiCl_4d_5-EB)_2$.

Isotopic congeners of (TiCl₄-EB)₂

Figure 4 gives FTIR spectra of parent, ¹⁸O-carbonyl and d_5 -ethyl (TiCl₄-EB)₂. Similar spectra were obtained for the two congeners with a deuterated phenyl ring, but these spectra were of lower quality and are not given here.

A very confusing pattern is seen for the changes in the α -C–O stretching frequency upon complexation (Fig. 7, Table 3). The change varies between +47 and +83 cm⁻¹ depending on which isotopic congener is considered, and there are considerable



Fig. 7. FTIR spectra at -196 °C for hydrogen/deuterium homologues of ethyl benzoate compared to their corresponding (TiCl₄EB)₂ complexes. "X" denotes a d_5 -benzoic acid impurity band. "*" is attributed to an titanium oxychloride impurity.

differences in the intensities of the α -C-O stretching bands. The situation is a clearcut example of a breakdown of a simplified assignment. The differences also demonstrate that utmost care is needed if one wants to correlate vibrational frequencies with any parameter. In this case the results will be highly dependent on which isotopic congener is considered.

The confusing behavior is due to a strong coupling between several vibrations, as can be seen from the increased frequency and intensity for several bands in the region $1300-1430 \text{ cm}^{-1}$. If we sum the shifts for the bands in two frequency ranges as in Table 3, we find a good overall agreement, except for Ed_5 -B. The discrepancy for the latter is due to the very low frequency for the α -C-O stretching vibration in the free ester (1254 cm⁻¹), and a wider frequency range has to be included to explain this case.

There is a general trend that the bands that are shifted most upon complexation have higher intensities than those who are less shifted. This trend can also be seen if we compare the spectra of the different complexes; the stronger the complexation, the higher the frequency and the higher the intensity of the ethyl deformation bands. In particular, the strength of the complexation can be directly correlated to the relative intensity of the methylene wag band $(1400-1420 \text{ cm}^{-1})$ relative to the methyl umbrella deformation (*ca* 1380 cm⁻¹) (see Fig. 3). This effect is due to an increase in the contribution of the α -C-O stretching mode in the potential energy of these vibrations.

Force field calculations

In order to verify the assignments, especially for the skeletal modes, a crude expansion of a force field developed for ethyl benzoate was performed. The expansion was too crude to justify tabulation of the results, but the qualitative fit to important frequencies and shifts was convincing.

The original ethyl benzoate force field [65] was developed from a slightly modified PULAY-FOGARASI-BOGGS benzene field [79] and a simplified

SNYDER-SCHACHTSCHNEIDER alkene field [80]. Only 29 parameters were refined, and a total of 190 observed frequencies for five isotopic homologues were modelled with a standard deviation less than 6 cm^{-1} .

In the expansion of the force field the following two changes were made: (a) a bromine atom was introduced to imitate the titanium tetrachloride entity, and a stretching force constant of 3.0 mdyn/Å for Br–O was introduced; (b) the C–O stretching force constants of the ester were adjusted according to experimental bonding lengths. The expansion of the field was performed with the program VIBFIT [81].

The bromine atom was assumed to make a relevant model for the titanium chloride unit, as it approximately equals the mass of one titanium plus one chlorine atom. The Br–O stretching force constant was set to 3.0 mdyn/Å to give a reasonable fit to the Ti–O stretching frequency at 536 cm⁻¹. The magnitude is also in accordance with what has been found for TiCl₄–acetone complexes [82]. No other force constants were introduced.

Stretching force constants are related to bonding lengths by a formula of the form $k = a/(r-b)^3$ [83, 84], k and r being the force constant and the bonding distance, respectively. The correlation is shown in Fig. 8 for the C-O stretching vibrations of the neat ester (bonding lengths from PEREZ and BRISSE [85-88]). The C-O bonding lengths in (TiCl₄-EB)₂ given by RYTTER *et al.* [26, 73] yielded force constants of 3.9, 7.4 and 9.9 mdyn/Å. The latter was too high to give a good fit, and a force constant of 9.3 mdyn/Å, corresponding to a bond length of *ca* 1.25 Å was used.

No other modifications of diagonal or off-diagonal force constants or geometry were done in the expansion of the force field.

The coupling between the C=O stretching vibration and one of the phenyl vibrations was predicted with a reasonably accurate magnitude, but the carbonyl stretching vibration was predicted to couple with the phenyl mode at 1603 cm^{-1} , and not with the one at 1585 cm^{-1} as observed. This misfit is discussed in detail elsewhere [89].

The calculations predicted an increase in the α -C-O stretching frequency roughly in agreement with the observations, and also predicted the coupling to the ethyl group deformations and the strong coupling to the d_5 -phenyl vibration at ca 1390 cm⁻¹. However, the calculations emphasized the coupling to the umbrella deformation more than to the methylene wag, while the opposite is observed.

The calculations predicted a shift of the skeletal mode at 1125 cm^{-1} of several tenths of cm⁻¹, and an ¹⁸O shift of -7 cm^{-1} in the complex. The mode at 877 cm⁻¹ was predicted to move to a lower frequency, whereas the 853 cm⁻¹ O-C=O scissoring was predicted to end up at *ca* 890 cm⁻¹. The other skeletal deformations were predicted to end up at *ca* 405 (-90), 350 (-40), 290 (-40), 240 (-30) and 75 (-10) cm⁻¹, the numbers in parentheses are shifts upon complexation. These predictions, and the predicted isotopic shifts, are all in good agreement with observations (see Tables 1 and 3).

The isotopic shifts for the Ti–O stretching vibration were predicted to be -8, -17, -2 and -27 cm^{-1} for the ¹⁸O-carbonyl, d_5 -ethyl, d_5 -phenyl and the d_{10} -ester, respectively, all predictions in excellent agreement with the experimental results.



Fig. 8. Correlation between bonding distance and stretching force constant for the C–O bonds in neat ethyl benzoate, and the estimated stretching force constants in (TiCl₄EB)₂.

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