X-Ray Absorption Spectroscopy Investigation on the Structure of Methyl Acrylate–TiCl$_4$ Complexes in Solution

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EXAFS and XANES spectra of methyl acrylate–TiCl$_4$ complexes in nitrobenzene show that the titanium atom is coordinated to two oxygen atoms and four chlorine atoms for any methyl acrylate/TiCl$_4$ ratio; furthermore, there is no free TiCl$_4$, so some carbonyls must be coordinated to two titanium atoms, as confirmed by IR spectroscopy; coordination increases the titanium–chlorine distance with regard to TiCl$_4$.

Carbonyl compounds easily coordinate to hard Lewis acids (AlCl$_3$, TiCl$_4$, SnCl$_4$, *etc.*) to form unstable complexes that are used as reactive intermediates in a great number of important organic reactions. The Lewis acid plays a catalytic role; furthermore, the selectivity of the reaction is also modified. This is very interesting in asymmetric reactions, particularly if a chiral Lewis acid is used as a catalyst. It is then clear that knowledge of the structure of the carbonyl–Lewis acid complexes is of prime importance for the understanding of reaction mechanisms and in the rational design of chiral Lewis acid catalysts.

Consequently, there is a lot of work dealing with the structure of these complexes.[1–7] X-Ray crystallography[1–3] provides detailed structural informaton, but the data obtained refer to the crystal structure and they must be extrapolated for the structure of the complex in solution. Spectroscopic (IR and NMR) studies in solution[3–7] provide information about the possible formation of chelate complexes and about the structure of the organic part of the complex. However, detailed information about the structure of the metal in these complexes is not obtained using these techniques. This information can be obtained from EXAFS and XANES experiments.[8,9]

The Diels–Alder reaction is one of the most important Lewis acid-catalysed organic reactions, which justifies the great interest in the study of enone–Lewis acid complexes.[1–5] In view of this, we decided to study the complexation between methyl acrylate, a benchmark dienophile, and TiCl$_4$.

Most Lewis acid-catalysed reactions are carried out in chlorinated solvents or in hydrocarbons. Unfortunately, chlorinated solvents are not transparent to EXAFS while due to the low solubility of the complexes it is not possible to perform measurements in hydrocarbon solutions. Therefore, we decided to use nitrobenzene, a low X-ray absorbing solvent with a weak coordinating ability, in which the complexes are soluble enough to carry out the experiments.

The possibility of the presence of nitrobenzene–TiCl$_4$ complexes was eliminated by ^{13}C NMR, given that the four signals of nitrobenzene do not change upon the addition of TiCl$_4$. When TiCl$_4$ solutions in nitrobenzene are left to stand for a long time, the precipitation of polymeric species is observed. However, X-ray absorption experiments are quite fast, and no precipitate was observed after any of the experiments described in this work.

The Ti K-edge X-ray absorption spectra were recorded at the LURE laboratory in Orsay. The storage ring DCI was operating at 1.8 GeV and the average beam current was 150 mA. A double Si(111) crystal was used as a monochromator and harmonic rejection was achieved by slightly detuning the two crystals. Cells with a thickness of 0.2 and 1 mm with Mylar windows were used.

The experimental EXAFS signal was extracted from the raw spectra following standard methods. Background removal was performed and the atomic absorption coefficient was determined by a low order polynomial fit of the spectra.

EXAFS spectra of methyl acrylate–TiCl$_4$ complexes with 0.25, 0.50, 0.75 and 1.00 TiCl$_4$: acrylate molar ratio have been analysed by curve fitting of the filtered first shell contribution to the EXAFS formula, using as amplitude and phase shifts the data extracted from the spectra of TiCl$_4$ (Ti–Cl interatomic distance = 2.19 Å, N = 4) and Ti(Pr^{i}O)$_4$ (Ti–O interatomic

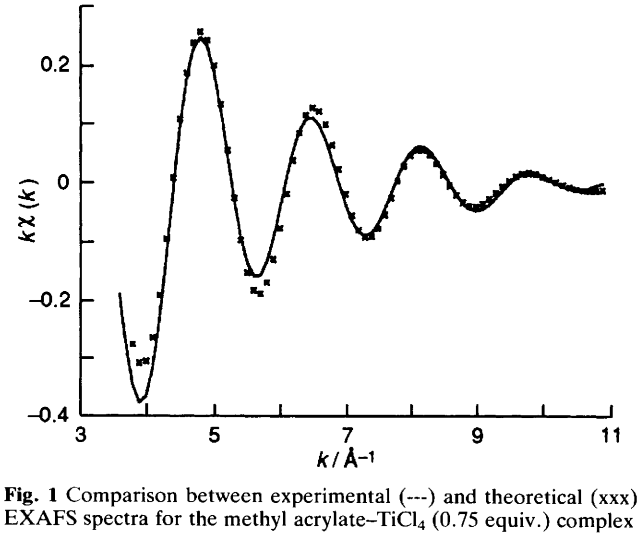

Fig. 1 Comparison between experimental (---) and theoretical (xxx) EXAFS spectra for the methyl acrylate–TiCl$_4$ (0.75 equiv.) complex

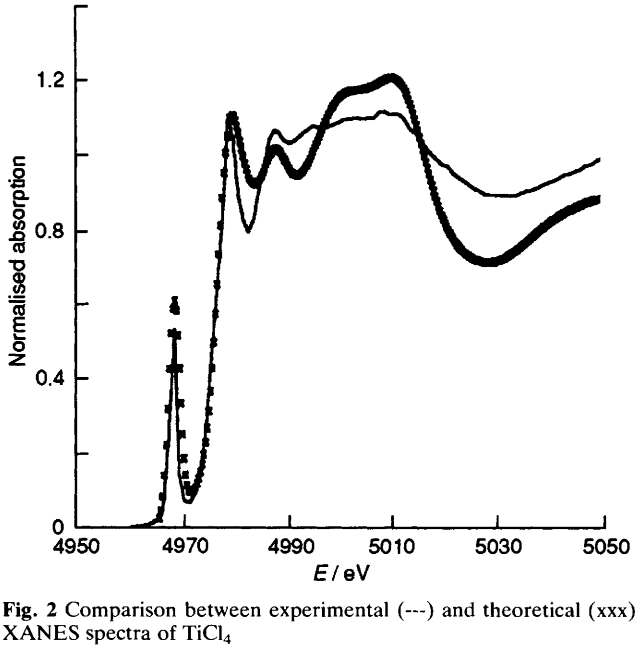

Fig. 2 Comparison between experimental (---) and theoretical (xxx) XANES spectra of TiCl$_4$

distance = 1.78 Å, N = 4) for the Ti–Cl and Ti–O contributions respectively. Coordination numbers N were fixed and fits performed with several different Ti–Cl and Ti–O multiplicity ratios. No second shell contribution have been detected. Fig. 1 shows an example of the fitting obtained with N(Ti–Cl) = 4 and N(Ti–O) = 2. All the fits performed with different N values were definitely worse than the 4/2 fit.

In methyl acrylate–$TiCl_4$ complexes, titanium atom is coordinated to four chlorine atoms (at 2.26 Å) and two oxygen atoms (at 2.13 Å), independently of the methyl acrylate/$TiCl_4$ ratio, Debye Waller differences range between 2×10^{-3} and 6×10^{-3} Å^2. This tendency to coordinate with two carbonyl groups has been experimentally shown for $TiCl_4$[7] complexes with aldehydes and in chelate complexes with $TiCl_4$.[1,5] This phenomenon has been explained by theoretical calculations of formaldehyde–$TiCl_4$ complexes.[10]

Normalised XANES spectra at the titanium K edge of all the methyl acrylate–$TiCl_4$ complexes are very similar and differ from that of $TiCl_4$, in particular the pre-peak structure is practically non-existent, which indicates the absence of free $TiCl_4$.

In order to determine the geometry of these complexes we have performed *ab initio* XANES calculations on the multiple scattering formalism for a tetrahedral $TiCl_4$ cluster (Fig. 2), a pentacoordinated titanium complex and two octahedral titanium complexes, with oxygen atoms in adjacent or apical positions. Computations have been carried out using the MSXAS program.[11] The experimental spectra are better reproduced by the calculations for octahedral symmetry, that show the three main resonances and no pre-peak. The accuracy of the calculations does not allow discrimination between the two possible octahedral complexes.

So, XANES also shows the existence of 2:1 methyl acrylate–$TiCl_4$ complexes. Furthermore, free $TiCl_4$ is not observed for any methyl acrylate/$TiCl_4$ ratio. The lack of free $TiCl_4$ for $TiCl_4$/methyl acrylate ratios greater than 0.5 indicates the simultaneous coordination of two titanium atoms to the same carbonyl groups leading to dimeric or polymeric species. A second shell Ti coordination would be expected but the large dynamic disorder together with the interference of Cl atoms at nearly the same distance makes it hard to be detected. IR spectroscopy provides direct evidence for this behaviour. In fact, the IR spectra of methyl acrylate in methylene chloride shows, in the presence of less than 1 equiv. of $TiCl_4$, three carbonyl stretching bands that can be assigned to the free-(1724 cm^{-1}), mono-(1652 cm^{-1}) and di-coordinated (1588 cm^{-1}) carbonyl groups. The band corresponding to the free carbonyl group disappears for an equimolecular methyl acrylate–$TiCl_4$ ratio.

In asymmetric Diels–Alder reactions of chiral acrylates, the use of Lewis acid catalysts increases the asymmetric induction by shifting the conformational (S)-*cis*/(S)-*trans* equilibrium of the acrylate towards the (S)-*trans* form.[12] Particularly interesting is the case of (−)-8-phenylmenthol acrylate, where the non-catalysed reaction takes place preferentially through the (S)-*cis* conformer.[13] Oppolzer *et al.*[14] have studied the reaction of this chiral dienophile with cyclopentadiene and have shown that the results obtained depend on the nature and the amount of catalyst, the best asymmetric induction being obtained in methylene chloride with 1.5 equiv. of $TiCl_4$.

The structural results described above show the coordination of two titanium atoms to the same carbonyl group. It seems logical that this dicoordination would greatly favour the (S)-*trans* conformer, which accounts for the higher asymmetric inductions obtained with larger amounts of $TiCl_4$. In order to corroborate this hypothesis, (−)-8-phenylmenthol acrylate was made to react with cyclopentadiene in the presence of two different proportions of $TiCl_4$. The diastereoisomeric excess increases from 85% to >99% in going from 0.25 to 0.75 equiv. of $TiCl_4$. The increase of the asymmetric induction with the amount of $TiCl_4$ agrees with the aforementioned hypothesis.

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