Short Communication

Positive Isotopic Shifts in Ethyl-$d_5$ Benzoate and Ethyl-1,1-$d_2$ Benzoate, and the Assignment of the $\alpha$–C–O Stretching Mode

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The strong band observed at ca. 1280 cm$^{-1}$ in the IR spectrum of ethyl benzoate, and at similar frequencies for several other organic esters, has been assigned as a skeletal stretching vibration because of its strong intensity. The main contributor to this vibration is the stretching of the $\alpha$–C–O bond, which is clearly evidenced from changes in the FTIR spectra of ethyl benzoate upon complexation with inorganic chlorides. A significant isotopic shift of ca. $-5$ cm$^{-1}$ when $^{18}$O is incorporated in the ether bridge supports this conclusion.

A positive isotopic shift observed upon deuteration of the ethyl group has, however, attracted attention and has led to alternative assignments of the $\alpha$–C–O stretching band. Similar positive shifts upon deuteration of the alkoxy group have also been reported for methyl acetate and methyl benzoate, among others.

During the last decades ethyl benzoate has been used as a complexing agent in Ziegler-Natta catalysts for the polymerization of propene. A number of papers have appeared describing the use of IR spectroscopy to keep track of ethyl benzoate during preparation of the catalysts, and to obtain information about the active site of the catalyst (see for instance Ref. 10). In this context, the correct interpretation of the $\alpha$–C–O stretching vibration is of crucial importance.

Experimental

Synthesis of 1,1-$d_2$-ethyl benzoate. To a slurry containing 2.5 g of LiAld$_4$ in 50 ml of dry ether was added dropwise 7.2 g of ethyl acetate at room temperature. The reaction mixture was stirred for 3 h and then 27.6 g of benzoyl chloride was added. The resulting reaction mixture was stirred overnight and NaF solution (1.0 M) was added. The mixture was filtered, and the filtrate was washed with $3\times50$ ml water, dried over anhydrous Na$_2$SO$_4$ and the solvent evaporated. The yield after distillation was 26.2 g (86%). The product exhibited the following spectroscopic properties: NMR (100 MHz, CDCl$_3$): $\delta$ 1.35 (t) and 1.34 (s) (3H), 4.28 (q) (1H), 7.3 (m) (3H), 7.9 (m) (2H) ppm. MS [IP 70 eV (m/z, %)]: 153 (12), 152 (95), 151 (13), 151 (100). These data are consistent with an approximately 1:1 mixture of ethyl-1,1-$d_2$ benzoate and parent ethyl benzoate. There was no indication of scrambling or monodeuteriation.

Ethyl-$d_5$ benzoate was synthesized from benzoyl chloride and anhydrous ethanol-$d_6$ (Stohler, USA, 99 % Isotopic purity) by standard methods. The pure product was dried over anhydrous sodium sulfate and distilled twice under vacuum.

The FTIR spectra were recorded for liquid samples between CsI windows on a Bruker IFS 113v FTIR spectrometer.

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Results

Fig. 1 shows the IR spectra of ethyl benzoate, ethyl-1,1-$d_2$ benzoate and ethyl-$d_5$ benzoate. Some selected frequencies are given in Table 1.

Discussion

The most important feature is the +18 cm$^{-1}$ isotopic shift upon deuteration of the whole ethyl group or specific deuteration of the methylene protons. The vibration is clearly a complicated mixture of several modes, but we still think that the band deserves assignment as an $\alpha$-C-O stretching band.

The positive, and apparently paradoxical, isotopic shift is probably due to mixing between the $\alpha$-C-O stretching mode and ethyl deformations (mainly methylene wag) in the parent ester. When the methyl deformations are shifted to lower frequencies upon deuteration the mixing is removed, and the skeletal mode is shifted to a higher frequency.

The mixing of the ethylene deformations and the $\alpha$-C-O stretching vibration is clearly demonstrated by the changes in IR spectra upon complexations with TiCl$_4$.\textsuperscript{6,7} For the parent ester there is an increase in the frequency of the $\alpha$-C-O stretching frequency of +53 cm$^{-1}$, whereas the corresponding shift for ethyl-$d_5$ benzoate is +83 cm$^{-1}$. This difference is, however, more than outweighed by an added shift of

![Fig. 1. FTIR spectra of a 1:1 mixture of ethyl benzoate and ethyl-1,1-$d_2$ benzoate (below) and ethyl-$d_5$ benzoate (above). P denotes the parent $\alpha$-C-O stretch.](image)

Table 1. Some selected IR frequencies for ethyl benzoate, ethyl-1,1-$d_2$ benzoate and ethyl-$d_5$ benzoate.\textsuperscript{*}

<table>
<thead>
<tr>
<th>Parent Ester</th>
<th>Ethyl-$d_2$ Complex</th>
<th>Ethyl-$d_5$ Complex</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1720 vs</td>
<td>1560 vs</td>
<td>1720 vs</td>
<td>Carbonyl stretch</td>
</tr>
<tr>
<td>1603 w</td>
<td>1600 sh</td>
<td>1603 w</td>
<td>Phenyl stretch</td>
</tr>
<tr>
<td>1585 w</td>
<td>1594 vs</td>
<td>1585 w</td>
<td>Phenyl stretch</td>
</tr>
<tr>
<td>1492 w</td>
<td>1494 w</td>
<td>1492 w</td>
<td>Phenyl stretch</td>
</tr>
<tr>
<td>1477 w</td>
<td>?</td>
<td>1477 w</td>
<td>Symmetric methyl wag</td>
</tr>
<tr>
<td>1465 w</td>
<td>1468 m</td>
<td>b</td>
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<tr>
<td>1451 m</td>
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<td>1417 s</td>
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<tr>
<td>1368 m</td>
<td>1383 s</td>
<td>b</td>
<td>Methyl umbrella</td>
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<tr>
<td>1314 s</td>
<td>1310 s</td>
<td>1317 s</td>
<td>Phenyl stretch</td>
</tr>
<tr>
<td>1277 vs</td>
<td>1333 s</td>
<td>1295 vs</td>
<td>$\alpha$-C-O stretch</td>
</tr>
</tbody>
</table>

\textsuperscript{*}All frequencies in cm$^{-1}$. All vibrations are in plane ($A'$) except for the antisymmetric methyl wag. Intensities are visual estimates: w = weak, m = medium, s = strong, vs = very strong, sh = shoulder. Complex denotes the equimolar titanium tetrachloride-ethyl benzoate complex.\textsuperscript{8} \textsuperscript{8}The corresponding vibration is found at frequencies below 1200 cm$^{-1}$.
40 cm\(^{-1}\) for the two ethyl deformations at 1368 and 1393 cm\(^{-1}\) in the parent liquid ester. The increased contribution from the skeletal mode in the ethyl deformations is also seen from the relative intensities. For the neat parent ester the \(\alpha-C-O\) stretching band is far more intense than the other two, whereas in the complex these three bands are of similar intensity.

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**References**


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