

Positive Isotopic Shifts in Ethyl- d_5 Benzoate and Ethyl-1,1- d_2 Benzoate, and the Assignment of the α -C-O Stretching Mode

Martin Ystenes,^{a,*} Per H. J. Carlsen^b and Erling Rytter^c

^aUniversity of Trondheim, The Norwegian Institute of Technology, Institute of Inorganic Chemistry, ^bUniversity of Trondheim, The Norwegian Institute of Technology Institute of Organic Chemistry, N-7034 Trondheim and ^cStatoil, N-7004 Trondheim, Norway

Ystenes, M., Carlsen, P. H. J. and Rytter, E., 1988. Positive Isotopic Shifts in Ethyl- d_5 Benzoate and Ethyl-1,1- d_2 Benzoate, and the Assignment of the α -C-O Stretching Mode. - Acta Chem. Scand., Ser. B 42: 254-256.

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 vibration¹⁻⁶ because of its strong intensity. The main contributor to this vibration is the stretching of the α -C-O bond, which is clearly evidenced from changes in the FTIR spectra of ethyl benzoate upon complexation with inorganic chlorides.⁶⁻¹¹ A significant isotopic shift of ca. -5 cm^{-1} when ^{18}O is incorporated in the ether bridge supports this conclusion.¹²

A positive isotopic shift observed upon deuteration of the ethyl group has, however, attracted attention and has led to alternative assignments of the α -C-O stretching band.¹³ Similar positive shifts upon deuteration of the alkoxy group have also been reported for methyl acetate¹⁴ and methyl benzoate,¹² 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 α -C-O stretching vibration is of crucial importance.

*To whom correspondence should be addressed.

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 3×50 ml water, dried over anhydrous Na_2SO_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): δ 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 mono-deuteration.

Ethyl- d_5 benzoate was synthesized from benzoyl chloride and anhydrous ethanol- d_6 (Stohler, USA, 99% isotopic purity) by standard methods.¹⁵ 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.

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 $+18\text{ cm}^{-1}$ 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 $\alpha\text{-C-O}$ stretching band.

The positive, and apparently paradoxical, isotopic shift is probably due to mixing between the $\alpha\text{-C-O}$ 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 $\alpha\text{-C-O}$ stretching vibration is clearly demonstrated by the changes in IR spectra upon complexations with TiCl_4 .^{6,7} For the parent ester there is an increase in the frequency of the $\alpha\text{-C-O}$ stretching frequency of $+53\text{ cm}^{-1}$,

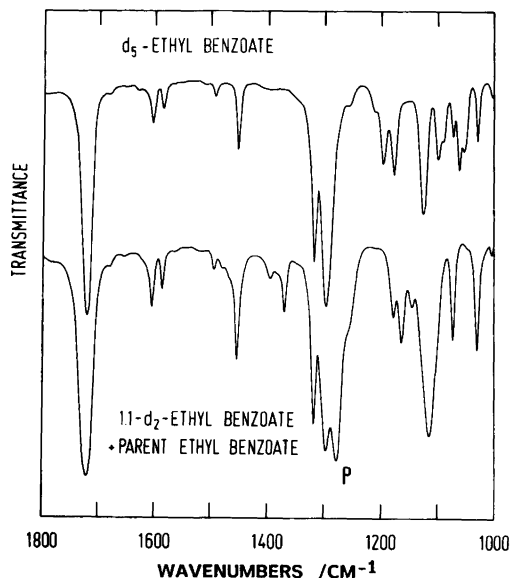


Fig. 1. FTIR spectra of a 1:1 mixture of ethyl benzoate and ethyl-1,1- d_2 benzoate (below) and ethyl- d_5 benzoate (above). P denotes the parent $\alpha\text{-C-O}$ stretch.

whereas the corresponding shift for ethyl- d_5 benzoate is $+83\text{ cm}^{-1}$. This difference is, however, more than outweighed by an added shift of

Table 1. Some selected IR frequencies for ethyl benzoate, ethyl-1,1- d_2 benzoate and ethyl- d_5 benzoate.^a

Parent		Ethyl- d_2	Ethyl- d_5		Assignment
Ester	Complex		Ester	Complex	
1720 vs	1560 vs	1720 vs	1720 vs	1560 vs	Carbonyl stretch
1603 w	1600 sh	1603 w	1603 w	1599 s	Phenyl stretch
1585 w	1594 vs	1585 w	1585 w	1595 sh	Phenyl stretch
1492 w	1494 w	1492 w	1492 w	1495 w	Phenyl stretch
1477 w	?	1477 w	<i>b</i>	<i>b</i>	Symmetric methyl wag
1465 w	1468 m	<i>b</i>	<i>b</i>	<i>b</i>	Methylene scissor
1451 m	1452 m	1451 m	1451 m	1452 m	Phenyl stretch
1447 sh	1445 w	1447 sh	<i>b</i>	<i>b</i>	Antisymmetric methyl wag
1393 m	1417 s	<i>b</i>	<i>b</i>	<i>b</i>	Methylene wag
1368 m	1383 s	≈ 1375 sh	<i>b</i>	<i>b</i>	Methyl umbrella
1314 s	1310 s	1317 s	1317 s	1315 s	Phenyl stretch
1277 vs	1333 s	1295 vs	1295 vs	1382 vs	$\alpha\text{-C-O}$ stretch

^aAll 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.⁸ ^bThe corresponding vibration is found at frequencies below 1200 cm^{-1} .

SHORT COMMUNICATION

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 $\alpha\text{-C-O}$ stretching band is far more intense than the other two, whereas in the complex these three bands are of similar intensity.

Acknowledgements. Financial support from *Norges Tekniske Høgskoles Fond* and Statoil is acknowledged.

References

1. Wilmshurst, J. K. *J. Mol. Spectrosc.* 1 (1957) 201.
2. Chattopadhyay, S. *Indian J. Phys.* 42 (1955) 335.
3. Hollenstein, H. and Gunthard, H. H. *J. Mol. Spectrosc.* 84 (1980) 457.
4. Green, J. H. S. and Harrison, D. J. *Spectrochim. Acta, Part A* 33 (1977) 583.
5. Ystenes, M. and Rytter, E. *Spectrochim. Acta. To be submitted.*
6. Ystenes, M. *Thesis No. 47*, Institute of Inorganic Chemistry, The Norwegian Institute of Technology, Trondheim, Norway 1986.
7. Ystenes, M. and Rytter, E. *Spectrochim. Acta. To be submitted.*
8. Ystenes, M. and Rytter, E. *Spectrosc. Lett.* 20 (1987) 519.
9. Rytter, E., Nirisen, Ø., Kvisle, S., Ystenes, M. and Øye, H. A. *Infrared Spectra, Bonding and Structure of the $\text{MgCl}_2/(\text{TiCl}_4 \cdot \text{EB})_2/\text{AlR}_3$ Catalytic System. Activation/Deactivation Kinetics of Propene Polymerization*, International Symposium on Transition Metal Catalyzed Polymerizations, Institute of Polymer Science, University of Akron, Ohio, USA 1986.
10. Chien, J. C. W., Wu, J. C. and Kuo, C. *J. Polym. Sci.* 20 (1982) 2019.
11. Spitz, R. and Lacombe, J. L. *J. Polym. Sci.* 22 (1984) 2611.
12. Carlsen, P. H. J. and Ystenes, M. *Acta Chem. Scand., Ser. B* 40 (1986) 757.
13. Boerio, F. J. and Bahl, S. K. *Spectrochim. Acta, Part A* 32 (1976) 987.
14. George, W. O., Houston, T. E. and Harris, W. C. *Spectrochim. Acta, Part A* 30 (1974) 1025.
15. Smith, B. U. and Waldron, N. M. *Vogel's Elementary Practical Organic Chemistry 1*, 3rd ed., Longman, London 1980.

Received January 29, 1988.