Conformations of Some Saturated Carbonyl Compounds. Part I. Infrared Spectra of Methyl Formate, Acetate, Propionate, and n-Butyrate; [$^2H_3$]Methyl Propionate and [$^2H_3$]Methyl n-Butyrate

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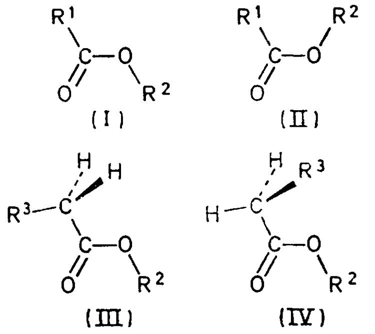
I.r. spectra of methyl formate. acetate. propionate. n-butyrate: and [$^2H_3$]methyl propionate and n-butyrate are reported. The effects of cooling solutions in carbon disulphide from 35 to −110°, and of solidification. on these spectra are interpreted in terms of conformational equilibria. One pair of conformers is suggested for methyl propionate for which the additional enthalpy ($\Delta H°$) for the high energy form is 87 ± 19 cal mol^{-1}. Two pairs of conformers are suggested for methyl n-butyrate for which the additional enthalpies of the high-energy forms are 92 ± 27 and 440 ± 20 cal mol^{-1}. It was not possible to determine $\Delta S°$ from the data.

A KNOWLEDGE of the conformations adopted by simple esters may help to relate bonding and non-bonding interactions to physical and chemical properties of this class of compounds. Possible conformations (I)—(IV) may exist. In simple esters, (I) is likely to be more stable than (II) because the dipole moment and the repulsion of oxygen lone-pair electrons are both minimised. Thus large enthalpy differences between (I) and (II) have been generally obtained from ultrasonic studies [1-3] on a range of esters, although a particular low value ($\Delta H° = 0{\cdot}4$ kcal mol^{-1}) for methyl formate by Bailey and North [3] would indicate the presence of an appreciable amount of (II) in equilibrium with (I); this would be in accord with interpretation of ultrasonic and i.r. data by Karpovich.[4] By contrast only (I) has been detected by dipole moment,[5] electron diffraction,[6] microwave, [7] and i.r.[8-10] studies. Oki and Nakanishi [10] provided i.r., dipole moment, and n.m.r. evidence for alkyl formates partially as (II) only when (I) is destabilized by bulky R^1 groups such as t-butyl, 1,1-diethylpropyl, and triphenylmethyl which lead to dominant repulsion forces between these groups and the carbonyl group.



SCHEME R^1 = H, Me, Et, or Pr^n, R^2 = Me, R^3 = Me or Et

Evidence has been noted [11] for equilibria of the type (III) $\rightleftharpoons$ (IV) on the basis of i.r. studies of esters of simple normal acids at various temperatures and analogous equilibria have been investigated in the case of esters of simple αβ-unsaturated acids.[12,13]

In the present work more detailed studies of integrated

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intensities of i.r. bands in methyl formate, acetate, propionate, and n-butyrate together with [$^2H_3$]methyl propionate and n-butyrate are made, using solutions in carbon disulphide at various temperatures between 35 and −110° and also using solidified solutions. The ΔH° values for (III) $\rightleftharpoons$ (IV) are redetermined for propionates and n-butyrates and evidence for an additional equilibrium is presented in the latter case. Attempts are also made to determine ΔS° values for these equilibria by methods[14,15] which have been applied to unsaturated esters.[13]

EXPERIMENTAL

I.r. spectra were measured using the same methods and conditions as described previously.[13]

Commercial samples of all esters were fractionally distilled and then purified chromatographically using a Wilkins Autoprep 705 instrument equipped with a 6-m Carbowax 20 M column at 100—120°.

[$^2H_3$]Methyl propionate was prepared by the dropwise addition of [$^2H_4$]methanol (3 ml) to freshly distilled propionyl chloride (12 ml) at 0°. The mixture was kept at 0° for 30 min and then refluxed for 3 h. The solution was cooled to 0° and then octan-1-ol (12 ml) was added to it; the mixture was then refluxed for 3 h. Finally the reaction mixture was fractionally distilled, the fractions in the range 85—95° being collected. The crude [$^2H_3$]-methyl propionate was purified using a Wilkins Autoprep 705 chromatograph equipped with a 6-m Carbowax 20 M column at 100°. [$^2H_3$]Methyl n-butyrate was prepared in a similar manner.

The purity of all samples was checked using a 2-m 5% PEGA column and a 1·5-m 10% Apiezon column at 60° in a Perkin-Elmer F11 chromatograph.

Samples were examined as solutions in carbon disulphide at 2% concentration in the 950—1400 cm^{-1} region and 15% in the 600—1000 cm^{-1} region at 0·1 mm path-length.

RESULTS AND DISCUSSION

The effects of temperature variation on the i.r. spectra of methyl and [$^2H_3$]methyl esters of saturated acids will be discussed for particular spectral regions where effects of conformational equilibria are apparent. The i.r. spectra of solutions of these esters at room temperature and at temperatures below which solidification occurs are presented in the Table. Assignments are restricted to particular conformers rather than to detailed normal modes of vibration for which detailed studies of Raman spectra are necessary.

1150—1250 *cm*$^{-1}$ *Region*.—Methyl propionate and n-butyrate each show a pair of bands near 1175 and 1196 cm^{-1} assigned to the antisymmetric C–C–O stretching mode for a high and low energy conformation respectively.[11] These assignments are crucial to structural studies of esters and merit further study. From the Table these pairs of bands are present in the spectra of the solidified solution of methyl propionate and n-butyrate although they tend to split and move to higher wavenumber. We consider that the high-energy conformer persists in the solid state. This is in contrast to studies on unsaturated esters;[13] analogous pairs of bands are observed near 1200 cm^{-1} but the low wavenumber component (high-energy conformer) is considered not to exist in the solidified sample. These tentative conclusions are supported by examination of the spectra of methyl acetate and methyl formate. Methyl acetate has a single intense band at 1240 cm^{-1}. Methyl formate has intense bands at 1158 and 1206 cm^{-1} which Karpovich assigns[4] to (II) and (I) respectively. However detailed studies of the i.r. spectra of deuteriated methyl formates by Suzi and Zell[9] suggest that these two bands are different normal modes of a single conformer in accordance with assignments by Wilmshurst[8] based on the contours of bands in the vapour state.

The i.r. wavenumber values (1400—600 cm^{-1}) of methyl formate, acetate, propionate and n-butyrate and [$^2H_3$]methyl propionate and n-butyrate as solutions in carbon disulphide at different temperatures 30 to −150°

Methyl formate: absent—1400w,sh, 1375w—1385w, absent—1380w, 1230vw,sh—1240vw,sh, 1206vs—1220vs,b, absent—1181m, absent—1168s, absent—1160m,sh, 1158vs—1175vs, 1096vw—1100vw,b, 1029w—1027vw, 1021w—1019vw,sh, absent—906vs,sh, 912s—900vs,sh, absent—773w,sh, 767m—769m

Methyl acetate: 1370s—1383s, absent—1367w, 1275m—1280m,sh, 1240vs—1250vs,b, 1186w—1186m, 1157w—1160vw, 1138w—1142vw, absent—1128vw, absent—1057vs, 1046s—1050vs, 980m—989m, absent—983w,sh, 843s—853vs, 782vw—795vw,b, 761vw—750vw,b, 640m—643m, 604m—617m

Methyl propionate: 1380w—1387w, 1353s—1362s, 1327vw—1327vw,sh, 1273w—1265vw, absent—1210vs, 1198vs—1202vs, 1176vs—1186vs, absent—1179vs, 1086m—1093m, absent—1026m,sh, 1022m—1023m, 967w—965m, 849m—856s, absent—812w,sh, 807m—808m, 656vw—653vw

[$^2H_3$]Methyl propionate: 1381vw,sh, 1390vw,sh, 1358s—1362m, 1327vw—1327vw,sh, 1283m—1263vw, absent—1215vs-, sh, 1207vs—1210vs, 1093vs—1093vs, absent—1088vs, absent—1068m, 1065vw,sh—1063m, 1035vw—1032w, 983m—985s, 940m—942s, 902vw—907vw, absent—900vw, 808m—806s, 653w—656w

Methyl n-butyrate: 1382m—1392s, 1358s—1380w, 1352m,sh—absent, 1307m—1310m, 1290m,sh—absent, 1260s—absent, 1236m,sh—absent, 1194vs—1202vs,b, 1174vs—1181vs,b, absent—1117m, 1108m,sh—1108m, 1098m—absent, 1082w,sh-—absent, 1052w—absent, 1040vw,sh—1040vw, 1007m,sh—absent, 998m—1001m,sh, absent—905m,sh, 901w—900s, absent—883m, 878w—877m, 864w—absent, 838w—absent, 795w,sh—absent, 787w—absent, 749w—749s, 703w—704s, 580vw—578w

[$^2H_3$]Methyl n-butyrate: 1382m,sh—1400s, 1363m—1375w,sh, 1353m,sh—absent, 1310m—1316s, 1288m,sh—absent, 1270s—absent, 1230m,sh—1230w,sh, 1198vs—1209vs,b, 1116m,sh—1119s, 1109m,sh—1109m, 1089vs—1087s, 1054w—1056w, 1047w, sh—1044m, 1022vw—1019m, 1007vw—absent, 964m—964s, 904w,sh—absent, 899w—894vs, 872vw—876vw, 837vw—836vw, 760w—absent, 749w,sh—749vs, 677vw—677s, 672vw,sh—672m,sh, 582w—576w

sh = Shoulder; s = strong; m = medium; w = weak; v = very; b = broad.

The intensities of certain i.r. bands (measured as

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integrated absorbances to include the band wings stretching over a wide wavenumber range) as a function of temperature are shown in Figure 1 for methyl propionate. It has been found[16] that there is a tendency for the integrated intensity of i.r. bands of carbonyl compounds to increase with decreasing temperature. Caution must, therefore, be exercised when determining thermodynamic parameters from these measurements; the testing of the various assumptions has been described for unsaturated esters.[13]

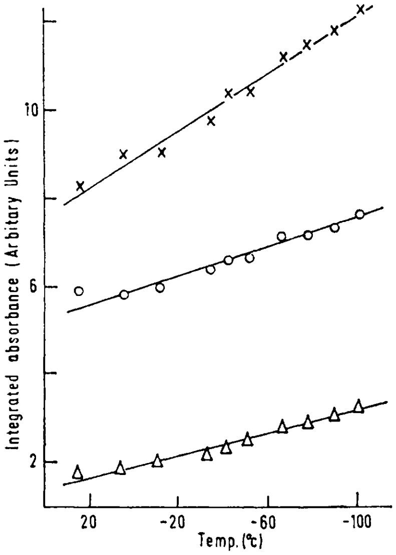

FIGURE 1 Integrated absorbance of bands in methyl propionate at 2% (v/v) in CS$_2$ and 0·1-mm path-length at different temperatures, × — 1198 cm^{-1}, ○ — 1176 cm^{-1}, △ — 1353 cm^{-1}

The integrated intensities of bands at 1176, 1198, and 1353 cm^{-1} in methyl propionate at different temperatures are given in Figure 1. The relative intensity changes for the pair at 1176 and 1198 cm^{-1} lead to a value of 87 ± 19 cal mol^{-1} for the additional enthalpy ($\Delta H^\circ \pm$ the standard deviation) of the less-stable conformer of methyl propionate in reasonable agreement with the value 78 ± 50 cal mol^{-1} made on the basis of peak-height measurements.[11] The band at 1353 cm^{-1} is assigned to a symmetric methyl deformation for which no conformational splitting is observed. It was therefore taken as a common band and attempts were made to calculate the difference in entropy between the conformers. These failed since it appeared that the assumptions in the methods of Mizushima *et al.*[14] and Hartman *et al.*[15] were not valid, in this case.

The changes in the integrated intensities of bands at 1174 and 1194 cm^{-1} in the i.r. spectrum of methyl n-butyrate are shown in Figure 2. The relative intensity changes of the pair at 1174 and 1194 cm^{-1} lead to a value of 92 ± 27 cal mol^{-1} for the additional enthalpy (ΔH°) of the less-stable conformer of methyl n-butyrate compared with 182 ± 60 cal mol^{-1} on the basis of peak-height measurement.[11] Attempts to measure the ΔS° value were unsuccessful.

The i.r. spectra of $[^2H_3]$methyl propionate and n-butyrate are presented in the Table. In each case only a single band is observed near 1200 cm^{-1} which splits and moves to higher wavenumber value in the solid. This is parallel to results for unsaturated esters[13] and suggests that conformational splitting of the 1200 cm^{-1} pair of bands in esters is associated with contributions from CH$_3$ deformation motions to the antisymmetric C–C–O stretching motion.

1230—1400 *cm*$^{-1}$ *Region.*—Changes of temperature produced no significant effects on the relative intensity of i.r. bands for methyl propionate or $[^2H_3]$methyl propionate. For methyl n-butyrate and $[^2H_3]$methyl n-butyrate a pair of bands near 1265 and 1310 cm^{-1} show changes in relative intensity with decreasing temperature. The former band weakens and disappears from the spectrum for the frozen solution. In addition bands near 1233 and 1290 cm^{-1} in the solution spectra of both n-butyrates disappeared from the spectra of the frozen solutions. These changes are attributed to a different conformational equilibrium to that discussed in relation to the 1150—1250 cm^{-1} region. Unfortunately, because of band overlap, it was not possible to determine a ΔH° value in this case.

600—1100 *cm*$^{-1}$ *Region.*—As in the 1230—1400 cm^{-1} region significant temperature effects were only observed in the spectra of methyl and $[^2H_3]$methyl n-butyrates. It is apparent in both isotopic species that a pair of bands in the 740—790 cm^{-1} region are associated with low and high energy conformers. The separation of this pair (749 and 787 cm^{-1}) is greater in the spectrum of methyl n-butyrate than in that of $[^2H_3]$methyl n-butyrate (749 and 760 cm.$^{-1}$). The relative freedom from overlap for the pair in methyl n-butyrate enabled the integrated absorbance values of these two bands to be measured as a function of temperature (Figure 3). These results lead to a value of $\Delta H^\circ = 440 \pm 20$ cal

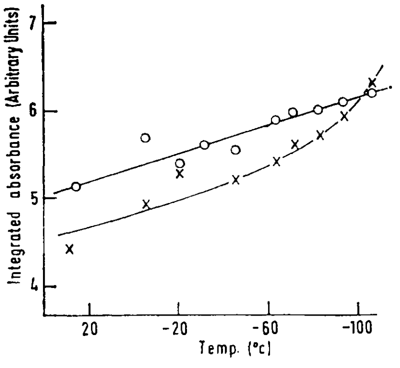

FIGURE 2 Integrated absorbance of bands in methyl n-butyrate at 2% (v/v) in CS$_2$ at 0·1-mm path-length at different temperatures, ○ — 1174 cm^{-1}, × — 1194 cm^{-1}

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[16] W. O. George, D. V. Hassid, and W. F. Maddams, to be published.

mol^{-1} for the equilibrium associated with these changes. Other bands in the spectra of solutions of n-butyrates and which are absent on solidification are listed in the Table and are probably also associated with the same high-energy conformer as the band at 749 cm^{-1}.

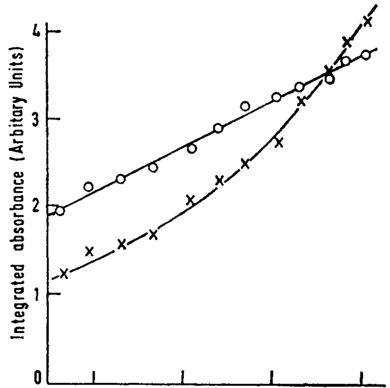

FIGURE 3 Integrated absorbance of bands in methyl n-butyrate at 15% (v/v) in CS_2 and 0·1-mm path-length at different temperatures, ○ — 787 cm^{-1}, × — 749 cm^{-1}

Conformation Equilibria.—The absence of two temperature-sensitive bands in the 1200 cm^{-1} region of methyl formate and acetate and the presence of two such bands in the spectra of methyl propionate and n-butyrate correlates with the absence of a three-fold barrier to internal rotation with different minima (this difference corresponding to $\Delta H°$) in the first two compounds and the presence of such a barrier in the second two compounds. Support for this correlation occurs in the observations by Jones *et al.*[17] and the band near 1240 cm^{-1} in a large number of 3-acetoxysteroids splits in certain cases into components which show relative intensity changes with temperature. These changes are tentatively associated[17] with isomers resulting from rotation about either of the C–O bonds. In the present work there is no evidence for a conformational equilibrium involving a two-fold barrier to internal rotation of the C–OR band [(I) $\rightleftharpoons$ (II)]. The changes in the 1200 cm.$^{-1}$ region provide evidence for a conformational equilibrium involving a three-fold rotation about the RCH_2–C bond [(III) $\rightleftharpoons$ (IV)].* The structure of (III) and (IV) cannot be established from the present work but rotational studies[19] on propionaldehyde suggest that generally the conformer in which a methyl group eclipses a carbonyl, (III), is more stable than the conformer in which these are gauche (IV).

The essential difference between the pairs of bands in the 1150—1250 cm^{-1} region and those in the other two regions for methyl and [$^2H_3$]methyl n-butyrates is that in the former case (as in the case of propionates) the band associated with the high-energy conformer persists in the frozen solution whereas in the latter cases the band associated with the high-energy conformer disappears. Certain other bands in the spectra of n-butyrates disappear on solidification (Table) and are probably associated with high-energy conformers although it is not clear where corresponding low-energy conformers absorb because of band overlap. We attribute these changes to an additional equilibrium with a greater $\Delta H°$ value than that associated with (III) $\rightleftharpoons$ (IV). This is presumably associated with the additional three-fold axis created by the terminal ethyl group in methyl n-butyrate.

Molecular models suggest that rotation of the βγ C–C bond is possible for certain orientations about the αβ C–C bond. However speculation about the nature of the various conformers possible in methyl n-butyrate lacks much factual evidence at this stage.

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* A recent paper[18] supports the existence of methyl n-propionate as conformers (III) $\rightleftharpoons$ (IV) on the basis of detailed studies of the carbonyl stretching vibrations.

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