Conformations of Esters of Saturated Normal Acids

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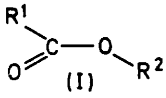
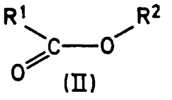
Summary Changes in the i.r. spectra of saturated esters between −110° and +40° suggest that in methyl propionate and methyl n-butyrate there is an equilibrium between the eclipsed and the gauche forms of the alkyl group with enthalpy (ΔH) differences between these forms of 78 ± 50 cal.mole^{-1} and 182 ± 60 cal.mole^{-1} respectively.

EVIDENCE is summarised in Table 1 for the existence of various saturated esters in conformations (I) to (VI).



(I)



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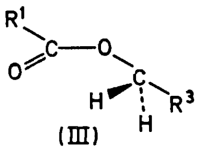
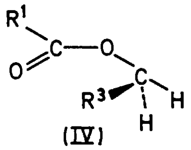
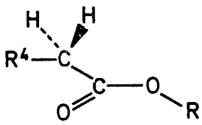


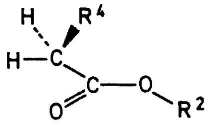
(III)



(IV)



(V)



(VI)

An analogous equilibrium to that suggested by Laato and Isotalo[8] for chloroacetates [(V) ⇌ (VI)] has been postulated for propionaldehyde by Butcher and Wilson[9] on the basis of microwave studies; it is considered that the gauche form is of higher energy than the eclipsed form in propionaldehyde.

In connection with a more general study of conformational equilibria, the effect of varying the temperature on the i.r. spectra of the methyl and ethyl esters of formic, acetic, propionic, and n-butyric acids was examined. In both methyl propionate and methyl butyrate a pair of bands near 1195 and 1175 cm^{-1} was found to be temperature dependent. In both cases the intensity of the higher-frequency band increases relative to the intensity of the lower frequency band as the temperature is decreased. The intensity measurements were made on the basis of peak heights. Assuming that the ester group remains in the *cis*-conformation by analogy with the acetates[3] and formates[1,2,6] the behaviour of these pairs of bands is taken to be evidence for an equilibrium between conformations (V and VI; R^4 = Me, Et; R^2 = Me). Each of these bands is assigned to a vibration of C–O and C–C bonds, and may be described approximately as an antisymmetric C–C–O stretching mode. The frequency of this vibration would be expected to be sensitive to the conformation at the α-carbon.

A doublet near 1200 cm.$^{-1}$ is observed in a number of other methyl esters of higher normal acids. In ethyl esters of normal acids there is a broad band near 1200 cm.$^{-1}$ which probably consists of several overlapping bands associated with various conformers. In particular a shoulder is observed at 1167 cm^{-1} in both ethyl propionate and ethyl n-butyrate.

TABLE 1

Conformations of saturated esters $R^1CO_2R^2$

R^1	R^2	Conformation	Method	Reference
H	Me	(I)	Microwave	1
			I.r.	2
Me	Me	(I)	Electron diffraction	3
n-$C_{17}H_{35}$	Et	(I)	Electron diffraction	4
F	Various alkyls	(II)	N.m.r. dipole moment	5
H	Et	(III) ⇌ (IV)	Microwave	6
Me	Various alkyls	(III) ⇌ (IV)	N.m.r.	7
CH_2Cl	Various alkyls	(V) ⇌ (VI)	I.r.	8

TABLE 2

Assigned antisymmetric C–C–O *stretching vibrations of the esters studied and the suggested conformational equilibria* (CS_2 *solution,* −110° *to* +40°)

	Antisym. C–C–O str. (cm^{-1})			Conformations	ΔH cal.mole^{-1} ± standard deviations)
Methyl formate		1206		(I)	
Methyl acetate		1241		(I)	
Methyl propionate ..	1199		1175	(V) ⇌ (VI)	78 ± 50
Methyl n-butyrate ..	1195		1175	(V) ⇌ (VI)	182 ± 60
Ethyl formate		1186		(III) ⇌ (IV)	
Ethyl acetate		1242		(III) ⇌ (IV)	
Ethyl propionate	1186		1167[a]	(III) ⇌ (IV) ⇌ (V) ⇌ (VI)	
Ethyl n-butyrate	1182		1167[a]	(III) ⇌ (IV) ⇌ (V) ⇌ (VI)	

[a] Too closely overlapped for temperature dependence studies.

Table 2 summarises the frequencies of the antisymmetric C–C–O stretching vibrations of the esters which have been studied, together with the conformations and equilibria suggested on the basis of previous studies (Table 1) and the present measurements. In the case of esters showing evidence for temperature-dependent equilibria, ΔH values have been estimated using methods described elsewhere.[10] Comparison with microwave results[9] for propionaldehyde suggests that the eclipsed form (V) is more stable than the gauche form (VI) in esters of saturated normal acids, although there is no direct evidence for this.

It should be emphasised that the absence of temperature-dependent effects is not positive evidence for the absence of conformational equilibria since the relevant bands may overlap or the ΔH values may be undetectably small in the temperature range studied.

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