Conformations of Some Saturated Carbonyl Compounds. Part III.[1] Infrared Spectra of Isomeric Propyl and Butyl Formates and Acetates

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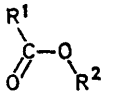
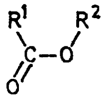
I.r. spectra of n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, and t-butyl formates and acetates are reported. The effects on these spectra of cooling liquid films and of solidification are interpreted in terms of conformational equilibria. Evidence for the presence of rotational equilibria has been obtained in all the esters except for isopropyl formate, isopropyl, and t-butyl acetate. Conformers are considered to arise from rotation about the HCO–O bond in t-butyl formate (for which ΔH° has been estimated as 150 ± 20 cal mol^{-1}) and from rotation about the O–alkyl bond in isobutyl formate (for which ΔH° has been estimated as 745 ± 40 cal mol^{-1}).

IN Part I [2] we related the i.r. spectra of a series of methyl esters to conformational equilibria due to rotation of the R^1–C bond. In Part II [1] we undertook a similar study of ethyl esters and found evidence for additional equilibria due to rotation of the O–R^2 bond. Enthalpy differences (ΔH°) between high and low energy conformers were reported in favourable cases. We now extend these studies to a series of formates and acetates with bulky R^2 substituents. Steric effects in t-butyl, 1,1-diethylpropyl, and triphenylmethyl formates were considered by Oki and Nakanishi [3] on the basis of i.r., n.m.r., and dipole moment measurements to destabilise (I) and form significant amounts of (II). Morgan and Unwin [4] have suggested the existence of (II) in isopropyl and t-butyl acetate, but this has not been supported by Oki and Nakanishi.[5] Our previous studies [1,2] provide a basis for discriminating between equilibrium (I) $\rightleftharpoons$ (II) and equilibria involving internal rotations within the R^1 and R^2 groups.



(I)



(II)

EXPERIMENTAL

The n-propyl and n-butyl formates and acetates used were commercial products. Other acetates were made from the alcohol and acetic anhydride in the presence of zinc chloride as described by Vogel.[6] Isopropyl, isobutyl, and s-butyl formates were prepared by refluxing anhydrous formic acid and the appropriate alcohol for 24 h. All these esters were distilled through a 25 cm packed column, the fraction at the f.p. of the ester being collected, and where necessary, this fraction was purified further by preparative chromatography. The t-butyl formate was prepared by the method

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[1] Part II, W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1972, 1798.

[2] W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1972, 1029.

[3] M. Oki and H. Nakanishi, *Bull. Chem. Soc. Japan*, 1970, **43**, 2558.

[4] K. J. Morgan and N. Unwin, *J. Chem. Soc.* (*B*), 1968, 880.

[5] M. Oki and H. Nakanishi, *Bull. Chem. Soc. Japan*, 1971, **44**, 3144.

[6] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 3rd edn., p. 384.

of Stevens and Van Es,[7] residual amounts of t-butanol and t-butyl acetate were removed by double passage through a 10% Apiezon L column (6 m) at 80 °C, a product of *ca.* 99% purity was obtained.

I.r. spectra were measured by use of the apparatus and procedures described.[8] Samples were examined as liquid capillary films, and where necessary at 0·1 mm thickness. Samples were annealed at various temperatures below the f.p. in order to obtain the most stable solidified form. The peak height absorbance measurements were obtained using an 0·3% solution in carbon disulphide at 0·15 mm path length for t-butyl formate, and a 50% solution in carbon disulphide at 0·15 mm for isobutyl formate.

RESULTS AND DISCUSSION

The effects of temperature variation on the i.r. spectra of the various chain-branched isomers of propyl and butyl formates and acetates will be discussed for each isomeric alkyl group. Spectra were recorded for both liquid films and solutions in carbon disulphide between +25 and −150 °C. Comparison of liquid and solution phases revealed no significant difference. The spectra of frozen liquid films were less affected by background scatter than those of frozen solutions and were unaffected by overlapping solvent absorptions. The liquid–solid spectra are presented in Supplementary Publication SUP No. 20673.* The solution spectra were used for the quantitative measurements.

For brevity certain pairs of bands will be described as conformer bands and the components will be described as high and low energy bands respectively in that order according to the criteria specified previously.[1]

n-Propyl Esters.—In the formate, conformer bands were observed at 936, 928; 900, 888; 743, 774; and 493, 462 cm^{-1}. These, and all other pairs, are listed as high and low energy bands respectively. In the case of the three lowest wavenumber pairs there is overlap with other bands which prevents the variation of intensity with temperature from being clearly seen. In the acetate, conformer bands were observed at 1066, 1047; 968, 911; and 837, 759 cm^{-1}.

Isopropyl Esters.—No conformer bands were detected by variable temperature studies.

n-Butyl Esters.—In the formate conformer bands were observed at 757, 774 and 466, 507 cm^{-1}. In the acetate conformer bands were observed at 1044, 1067; 752, 738; and 483, 508 cm^{-1}. Also a pair of bands at 1067, 1059 cm^{-1} in the spectrum of n-butyl formate appeared to be temperature dependent, but the former band persisted in the spectrum of the solidified sample and it is uncertain whether the 1067, 1059 cm^{-1} pair are conformer bands. Other bands of liquids absent in the spectra of the solidified state may be conformer bands but the identity of the low energy band is obscure in each case.

Isobutyl Esters.—In the formate, conformer bands were observed at 826, 846 and 486, 430 cm^{-1}. The former pair was used for quantitative measurements which are described later. In the acetate it was not possible to obtain a crystalline solid. It appeared that isobutyl acetate forms a supercooled liquid or glass which did not crystallise even after repeated annealing. However a pair of bands at 945, 927 cm^{-1} showed a systematic change in relative intensity with cooling and are probably conformer bands.

s-Butyl Esters.—In the formate, conformer bands were observed at 1094, 1113 and 863, 873 cm^{-1}. A pair of bands at 984, 997 cm^{-1} are probably conformer bands; overlaps restrict confirmation. The behaviour of the acetate resembled that of isobutyl acetate. A pair of bands at 1097, 1117 cm^{-1} are probably conformer bands. This would be confirmed if the 1097 cm^{-1} band disappeared from the spectrum of a crystalline solid. Repeated efforts failed to achieve the crystalline state.

t-Butyl Esters.—In the formate, Owen and Sheppard[9] found no evidence for conformational equilibria by variable temperature i.r.

Oki and Nakanishi[3] have commented that bands at 916, 574, and 435 cm^{-1} decrease as the temperature is lowered whereas those at 1020, 483, 409, and 242 cm^{-1} increase. These changes were observed in both liquid and gaseous phases.[3]

In the present work, the bands at 916 and 574 cm^{-1} were absent from the spectrum of the solid state but the band at 435 cm^{-1} persisted in the solid. A very weak shoulder at 1020 cm^{-1} in the liquid was absent in the solid but another weak shoulder at 1028 cm^{-1} in the solid was absent in the liquid. Oki and Nakanishi[3] limited their studies to the region 1100—200 cm^{-1}. We find apparent conformer bands at 1210, 1160 cm^{-1} on which quantitative intensity measurements were made.

In the acetate no conformer bands were detected. A weak band at 633 cm^{-1} weakened further. The solid state spectrum reveals significant difference from previously reported spectra[5] which are attributed to a more stable form occurring after prolonged annealing.

Conformational Equilibria.—The basis of the selection of the compounds studied in the present work is that internal rotations must either involve the R^1CO-OR^2 bond, the $O-R^2$ bond or internal rotations of the R^2 group. In the case of t-butyl formate, R^2 may be regarded as isotropic leaving only one possible axis for internal rotation corresponding to the equilibrium (I) $\rightleftharpoons$ (II). Oki and Nakanishi[3] report a value of 2·2 ± 0·7 kcal mol^{-1} for the enthalpy difference based on n.m.r. measurements.

In the present work we have attempted to measure this enthalpy difference from the conformer pair at 1210, 1160 cm^{-1}. Overlap precluded accurate integrated area measurements but peak height measurements were made, and using the methods and assumptions outlined previously,[8] a value $\Delta H^\circ = 150 \pm 20$ cal mol^{-1} was obtained as the mean of three sets of measurements, each involving 12 temperatures between +20 and −110 °C. The

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* For details of Supplementary Publications see Notice to Authors No 7 in *J. Chem. Soc. (A)*, 1970, Issue 20. (Items less than 10 pp. are supplied as full-size copies.)

[7] W. Stevens and A. Van Es, *Rec. Trav. chim.*, 1964, **83**, 1287.

[8] W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1972, 400.

[9] N. L. Owen and N. Sheppard, *Proc. Chem. Soc.*, 1963, 264.

discrepancy between the value determined by i.r. and that determined by n.m.r. is very large. There is no obvious explanation and clearly the assumptions used in each method require questioning.

Considering compounds possessing other axes for internal rotation the conformer bands at 826, 846 cm^{-1} in isobutyl formate were suitable for quantitative measurement on the basis of peak heights and provided a value of $\Delta H^\circ = 745 \pm 40$ cal mol^{-1}. The rotational motions associated with this change in enthalpy could be associated with the $HCO{-}OCH_2CHMe_2$ bond, the $HCOO{-}CH_2CHMe_2$ bond or the $HCOOCH_2{-}CHMe_2$ bond. Similar equilibria probably occur in the spectrum of isobutyl acetate. Comparisons within the present series of compounds suggest the second possibility is the most likely. Evidence for conformational equilibria also exists in the n-propyl, n-butyl, and s-butyl esters. Comparison with spectra of propionates and butyrates suggest these equilibria probably involve rotations within the alkyl chains.

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