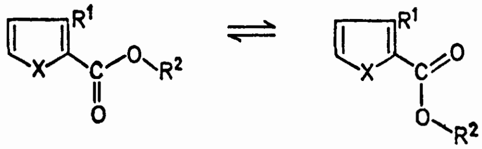
Determination of the Energy Differences between the Rotameric Forms of Furan and Thiophen Esters in Carbon Tetrachloride Solution by Infrared Spectrometry

By **D. J. Chadwick, J. Chambers, G. D. Meakins,*** and **R. L. Snowden,** Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

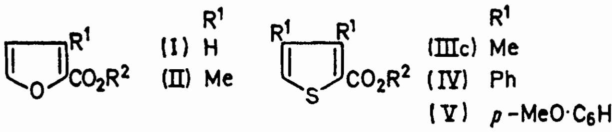
Practical and theoretical aspects of the Title subject are discussed. Study of the temperature variation of the rotamers' carbonyl bands gives reliable enthalpy differences. The variation of the dielectric constant of the solvent with temperature does not significantly affect these values. Entropy differences are more difficult to assess: an attempt to allow for possible differences in the absorption coefficients of the rotamers gives results which are appreciably different from, and less acceptable than, those obtained by assuming the coefficients to be equal. The values based on this assumption lead to the tentative conclusion that the thermochemically less stable forms of several of the esters predominate in carbon tetrachloride at room temperature.

VARIOUS effects may lead to the occurrence of two or more carbonyl bands in the spectra of compounds containing only one C=O group.[1] It is usually easy to decide between inter- and intra-molecular factors as the reason for multiple absorptions, but further distinction within the latter type is more difficult. In general a purely spectrometric approach will not differentiate unambiguously between rotational isomerism (*i.e.* the presence of more than one conformation) and Fermi resonance: comparison of the substrates with isotopically labelled analogues is required for this purpose.[2] Although several authentic cases of internal rotation in carbonyl compounds have been detected by i.r. spectrometry,[3a] little quantitative work has been reported, and the proportions of rotational isomers have generally been studied by n.m.r. spectrometry.[3b] Where energy differences rather than energy barriers are to be investigated, certain advantages (*e.g.* higher accuracy of relative intensity measurements) accrue from using the i.r. rather than the n.m.r. method.

SCHEME Energy differences and equilibrium constants for



Esters with a; R^2 = Me, b; R^2 = Et, c; R^2 = Bu^t derived from:



The statistical errors for enthalpy and free-energy differences (which are in J mol^{-1}) are ± 250, those for entropy differences (J K^{-1} mol^{-1}) are $\pm 1{\cdot}7$, and the equilibrium constants are accurate to $\pm 8\%$. The symbols used below are explained in the text. $\Delta G°$ and K values refer to 303 K. The $\Delta S°$, $\Delta G°$, and K values are based on the assumption that pairs of rotamers have equal absorption coefficients (*i.e.* α_l/α_h = 1; see text).

Ester	(Ia)	(Ib)	(Ic)	(IIa)	(IIb)	(IIc)	(IIIc)	(IVa)	(IVb)	(IVc)	(Va)	(Vb)	(Vc)
$\Delta H°$	−891	−1910	−2470	−2240	−963	−2640	2710	3060	−1050	1320	3830	2080	840
$\Delta S°$	−4·22	−9·04	−6·23	−3·91	4·22	−5·07	−1·40	6·80	−4·31	8·32	8·53	4·34	4·85
$\Delta G°_{303}$	325	796	−630	−1020	−2205	−1150	3080	1060	250	−1140	1270	810	−590
K_{303}	0·88	0·73	1·3	1·8	2·4	1·6	0·30	0·66	0·90	1·6	0·605	0·74	1·3

The esters studied here are shown in the Scheme. [The constants of the six known esters, and the preparations of the new furan derivatives (IIb and c), are given in the Experimental section; the new thiophen esters are described elsewhere.[4]] In dilute solution in carbon tetrachloride all these esters show well defined carbonyl doublets (see Figure). Deuteriated analogues,[5] the subject of a later paper, have similar doublets, thus suggesting that the bands arise from rotameric forms. This paper is concerned with the details of the i.r. approach to measuring energy differences between rotamers: for convenience specific structures[6] for the rotamers are shown in the Scheme, but the structural

---

[1] L. J. Bellamy, ' Advances in Infrared Group Frequencies,' Methuen, London, 1968.

[2] *Inter alia*, P. Yates, G. D. Abrams, and L. L. Williams, *Tetrahedron Letters*, 1969, **4341**; C. L. Angell, P. J. Krueger, R. Lauzon, L. C. Leitch, K. Noack, R. J. D. Smith, and R. N. Jones, *Spectrochim. Acta*, 1959, **11**, 926; G. Allen, P. S. Ellington, and G. D. Meakins, *J. Chem. Soc.*, 1960, 1909.

[3] (*a*) See, *e.g.*, K. Noack and R. N. Jones, *Canad. J. Chem.*, 1961, **39**, 2225; T. L. Brown, *Spectrochim. Acta*, 1962, **18**, 1615; H. Laato, *Ann. Univ. Turkuensis, Ser. A*, 1965, **86**, 3; C. K. Tseng, J. H. Chan, D. R. Baker, and F. H. Walker, *Tetrahedron Letters*, 1971, 3053; (*b*) see, *e.g.*, G. J. Karabatsos and D. J. Fenoglio, *J. Amer. Chem. Soc.*, 1969, **91**, 1124, 3572, 3577.

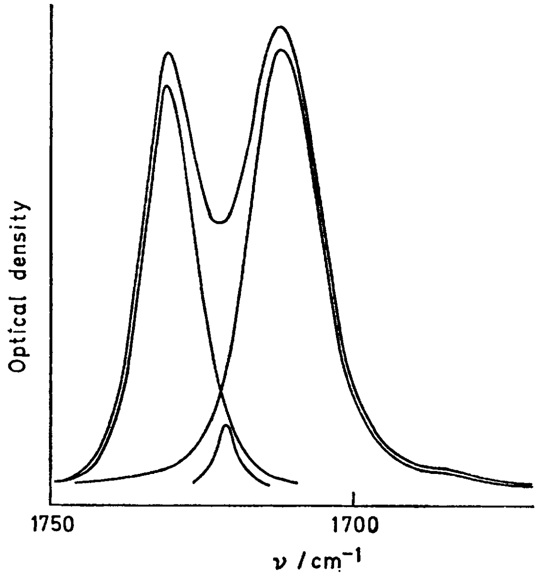
[4] D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin I*, 1972, 2079.

[5] D. J. Chadwick, D.Phil. Thesis, Oxford, 1972.

[6] D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *Chem. Comm.*, 1971, 625.

details and the correlation of particular structures with the doublets' components are not germane to the present study.

Preliminary experiments showed that reliable quantitative work with carbonyl bands requires spectra of high quality, free from the effects of absorption by moisture in the solutions or by atmospheric water vapour. The procedure adopted was to examine dry solutions of the compounds in carbon tetrachloride from 1800 to 1600 cm^{-1} on a high-resolution spectrometer purged continuously with dry air. Examinations were carried out (i) at different concentrations and constant temperature, (ii) at a fixed initial concentration over a range of temperatures, and (iii), for three esters, at constant concentration and temperature but with the solvent containing increasing amounts of acetonitrile. A complete spectrometric record is given for one compound, t-butyl furoate (Table 1), and the main features of all the esters' spectra are recorded in Table 3; the thermodynamic results obtained by the procedures explained in the following sections are shown in the Scheme.



Carbonyl absorption of t-butyl 2-furoate (Ic)

Although the maxima of the doublets are separated by *ca.* 15—20 cm^{-1}, each of the observed bands represents composite absorption by two components. Accurate (rather than merely ' graphical ') separation of the doublets into their components was therefore required as the basis of a quantitative treatment. Resolution of overlapping absorptions is best achieved by computer methods, provided that the mathematical form of the component bands is known. The shape of an isolated i.r. band has been treated in detail by Jones and Seshadri.[7] Bands of condensed state systems are basically of a Lorentzian form on which physical and instrumental factors impose a Gaussian perturbation. The most general approach is to consider the contribution of radiation with wavenumber ν_i to the intensity measured at a spectrometer setting of wavenumber ν. If the true absorption band is represented as $g(\nu)$, and the instrument function as $k(\nu - \nu_i)$, then the folding integral of the band profile is given by the Voigt convolution:

$$f(\nu) = \int_{-\infty}^{+\infty} g(\nu_i) \,.\, k(\nu - \nu_i)d\nu_i$$

From the tables of Davies and Vaughan [8] the fractions of the Lorentzian and Gaussian contributions to the profile of such a convolution can be determined from the ratios of the band widths at specific height fractions to the width at half height (*i.e.* the half-intensity band width). In the present study the C=O absorptions were resolved with an analogue computer to give symmetrical components whose composites filled the experimental traces closely. All the components were similar in form, as would be expected for i.r. bands of common vibrational origin, and the extent of Lorentzian character (*ca.* 70%) is reasonable from theoretical considerations.[7]

The purpose of the type (i) examinations (varying concentration) was to establish that the doublets were not influenced by solute–solute or solute–solvent interactions. In all cases the relative intensities of the doublets' components were independent of concentration even when this exceeded the value used in the other types of examination. [The results are given only for ester (Ic); for comparison the behaviour of bands associated with the ' monomer–dimer ' system of acetic acid is recorded in Table 1.]

The type (ii) examinations are concerned with the temperature dependence of the components' intensities. Handling the results requires consideration of the quantitative aspects of i.r. intensity data, which may be approached along the lines of Hartman *et al.*[9] as follows. Suppose an i.r. cell (path length p) contains a solution [concentration c (g l^{-1})] at temperature T (K) of a compound which exists as a mixture of two stable rotational isomers each having a characteristic carbonyl band suitable for intensity measurement. For the equilibrium:

$$h \text{ (form with higher C=O frequency)} \rightleftharpoons l \text{ (form with lower C=O frequency)}$$

let A_h = area of the band of rotamer h (*i.e.* a quantity proportional to the intensity of the band), α_h = integrated absorption coefficient of rotamer h, c_h = concentration (g l^{-1}) of rotamer h, K = equilibrium constant (c_l/c_h), ΔH° and ΔS° = enthalpy and entropy changes, respectively, for the conversion $h \rightleftharpoons l$. If the barrier to rotation is small compared with thermal energy,

$$K = A_l\alpha_h/A_h\alpha_l \quad (1)$$

$$\log (A_l/A_h) = (-\Delta H^\circ/2{\cdot}303RT) + (\Delta S^\circ/2{\cdot}303R) + \log (\alpha_l/\alpha_h) \quad (2)$$

$$A_l = -(\alpha_l/\alpha_h)A_h + \alpha_l pc \quad (3)$$

[7] R. N. Jones and K. Seshadri, *Spectrochim. Acta*, 1963, **19**, 1013.

[8] J. T. Davies and J. Vaughan, *Astrophysical J.*, 1963, **137**, 1302.

[9] K. O. Hartman, G. L. Carlson, R. E. Witkowski, and W. G. Fately, *Spectrochim. Acta*, 1968, **24***A*, 157.

Unless stated otherwise the following apply to all Tables. The solvent was CCl_4. Concentrations (c) are in mg per g of solvent, and temperatures (T) in K. The positions (in cm^{-1}), half-intensity band widths (in cm^{-1}), areas (in percentages), and optical densities of bands are denoted by ν, $\Delta\nu_{\frac{1}{2}}$, A, and D, respectively. The forms with higher and lower C=O frequencies are represented by the letters h and l. The abbreviation crc indicates the correlation coefficient of the regression specified.

TABLE 1

Detailed results with t-butyl 2-furoate (Ic)

Examination (i), at 293 K

c	8·39	1·45	0·82	0·084
A_l/A_h	1·33	1·31	1·31	1·32
D_l/D_h	0·98	0·97	0·96	0·97

AcOH ν_h 1765·5, ν_l 1712·5

c	3·40	0·34	0·03
D_l/D_h	20·7	5·5	1·6

Examination (ii), c 1·45

T	258	273	288	303	318	333	348
ν_h	1727·8	1728·3	1728·8	1729·4	1729·8	1730·2	1730·6
ν_l	1709·6	1710·2	1710·9	1712·6	1712·0	1712·4	1711·6
A_h	40·0	40·5	40·5	40·5	41·0	41·0	41·5
A_l	60·0	57·0	53·5	52·0	48·0	47·5	46·5
$\log_{10}(A_l/A_h)$	0·176	0·148	0·121	0·109	0·068	0·064	0·049
Total A	100·0	97·5	94·0	92·5	89·0	88·5	88·0
D_h	0·75	0·75	0·74	0·74	0·73	0·72	0·72
D_l	0·78	0·76	0·73	0·71	0·69	0·68	0·67
$\log_{10}(D_l/D_h)$	0·017	0·006	−0·006	−0·018	−0·024	−0·025	−0·031

Regression	$\log_{10}(A_l/A_h)$ *vs.* $1/T$	A_h *vs.* A_l	$\log_{10}(D_l/D_h)$ *vs.* $1/T$	D_h *vs.* D_l
Slope	129·10	−0·088	48·54	0·291
crc	0·990	−0·923	0·984	0·951

The D figures lead to $\Delta H^\circ - 929$, $(\Delta S^\circ)' - 3{\cdot}32$, $(\Delta G^\circ)'_{303} + 105$, K'_{303} 0·959 (see Scheme for values based on A figures)

Examination (iii), at 288 K

Solvent CCl_4(mol)	1·000	1·000	1·000	1·000	1·000
Solvent MeCN(mol)	0·000	0·055	0·093	0·135	0·329
ε	2·25	3·00	3·50	4·00	6·25
A_h	40·5	43·0	45·0	46·0	52·5
A_l	53·5	49·5	47·5	44·0	36·5
$\log_{10}(A_l/A_h)$	0·121	0·061	0·023	−0·019	−0·158

TABLE 2

Experiments on ' natural decrease ' (see text)

Solution containing 5α-androstan-3-one (ν_{285} 1713, c 1·721). Values of D, A, $\Delta\nu_{\frac{1}{2}}$, and c_r are relative to values at 248° taken as unity; c_r is a measure of the amount of solute in the light path calculated from the expansion of CCl_4.

T	D	A	$\Delta\nu_{\frac{1}{2}}$	c_r	T	D	A	$\Delta\nu_{\frac{1}{2}}$	c_r
248	1·00	1·00	1·00	1·00	313	0·84	0·88	1·08	0·93
273	0·92	0·91	1·04	0·97	333	0·79	0·84	1·10	0·90
290	0·88	0·88	1·07	0·95	353	0·73	0·80	1·11	0·88

Solution containing 5α-androstan-3-one (c 1·975), denoted by superscript x, and acetophenone (ν_{285} 1689·5, c 0·602), denoted by superscript y. $A^x + A^y$ is taken as 100 at 285 K. The subscript r indicates a value relative to that at 285 K taken as unity.

T	D^x	D_r^x	D^y	D_r^y	D^x/D^y	A^x	A_r^x	A^y	A_r^y	A^x/A^y
285	0·629	1·00	0·518	1·00	1·21	65·5	1·00	34·5	1·00	1·90
298	0·602	0·96	0·492	0·95	1·22	66·0	1·01	34·0	0·99	1·94
313	0·584	0·93	0·477	0·92	1·22	62·0	0·95	32·5	0·94	1·91
328	0·558	0·89	0·449	0·87	1·24	60·5	0·92	31·0	0·90	1·95
343	0·545	0·87	0·433	0·84	1·26	59·5	0·91	31·0	0·90	1·92

TABLE 3

Outline of results with the series of esters

	Ester	(Ia)	(Ib)	(Ic)	(IIa)	(IIb)	(1Ic)	(IIIc)	(1Va)	(IVb)	(IVc)	(Va)	(Vb)	(Vc)
At 258 K	ν_h	1738·5	1732·0	1729·0	1728·0	1725·5	1721·0	1703·5	1725·0	1722·5	1717·5	1725·5	1720·0	1714·5
	ν_l	1724·0	1716·0	1709·6	1712·5	1709·0	1704·0	1690·0	1698·0	1696·0	1692·0	1696·5	1693·0	1689·0
	A_h	49·0	55·0	40·0	35·5	20·5	35·0	81·0	59·0	50·5	39·0	64·0	57·5	45·0
	A_l	43·0	45·0	60·0	64·0	54·5	63·0	19·0	33·0	49·5	57·0	30·0	36·5	54·0
	$\log_{10}(A_l/A_h)$	−0·057	−0·087	0·176	0·255	0·425	0·255	−0·629	−0·253	−0·009	0·165	−0·329	−0·197	0·079
At 348 K	ν_h	1742·0	1735·0	1730·6	1734·5	1730·0	1724·5	1707·0	1731·0	1725·5	1720·0	1729·0	1723·0	1718·0
	ν_l	1726·5	1719·5	1712·8	1716·0	1712·5	1707·0	1694·0	1705·0	1701·5	1696·0	1703·0	1699·0	1692·5
	A_h	44·0	52·5	41·5	37·0	19·0	39·0	60·0	47·5	43·0	31·0	49·5	43·0	35·0
	A_l	35·0	34·0	46·5	51·0	44·5	52·0	20·0	38·5	37·0	53·0	38·0	36·0	47·0
	$\log_{10}(A_l/A_h)$	−0·100	−0·189	0·049	0·140	0·370	0·125	−0·478	−0·091	−0·066	0·233	−0·115	−0·077	0·128
Regression of $\log_{10}(A_l/A_h)$ *vs.* $1/T$	Slope	46·54	99·57	129·10	116·9	50·33	137·8	−141·54	−159·9	54·98	−68·89	−119·8	−108·9	−43·90
	crc	0·791	0·995	0·990	0·991	0·936	0·984	−0·991	−0·989	0·992	−0·990	−0·990	−0·991	−0·993
Regression of A_h *vs.* A_l	Slope	0·582	0·239	−0·088	−0·129	0·151	−0·42	−11·26	−2·49	0·638	1·98	−1·76	4·91	1·33
	crc	0·919	0·960	−0·923	−0·924	0·922	−0·972	−0·841	−0·934	0·990	0·949	−0·940	0·704	0·997

Application of equation (2) to the results of variable temperature runs affords ΔH° if ΔS° and the *ratio* α_l/α_h are independent of temperature. To find K, from equation (1), this ratio must be known. If the α *values* are assumed to be independent of temperature, the ratio can be found, from equation (3), by a plot of A_l *versus* A_h at different temperatures. The value of K gives ΔG°, the free energy change for $h \rightleftharpoons l$, and ΔS° follows since ΔH° is known.

To test some of the assumptions involved in this approach the experiments leading to the results in Table 2 were carried out. 5α-Androstan-3-one gives an almost symmetrical carbonyl band: the optical density and the area of the band decrease as the temperature increases (Table 2). In the temperature range used the expansion of the cell was negligible and the calculated expansion of the solution would account for less than half of the observed effect. Mierzecki[10] found a similar decrease in the extinction coefficients of certain bands of aromatic compounds: in the present case the band becomes weaker no matter what criterion of intensity is considered. Heating a cell filled with solvent did not cause any change in the base-line absorption, indicating that the effect does not arise from an increase in secondary emission at higher temperature. Although the origin of the ' natural decrease ' remains obscure it appears to occur with a variety of i.r. bands,[10] and to assume that the α *values* of the heterocyclic compounds' carbonyl bands are independent of temperature is clearly unjustified. However, such an assumption for the α *ratios* appears to be reasonable: when a mixture of the two carbonyl compounds, each having one carbonyl band, was heated both bands showed natural decrease, but the ratio of the band areas did not change appreciably (Table 2).

In order to circumvent the difficulties arising from this effect, A_l/A_h *ratios* were used in the present work. Plots of $\log_{10}(A_l/A_h)$ versus $1/T$ gave the ΔH° figures in the Scheme. [All linear plots of two variables were made by linear regression analysis using magnetic card program storage. The Tables show the correlation coefficients, which reflect the closeness of the best least square plots to the experimental data. Small frequency shifts, to higher values with increasing temperature, were observed generally with the carbonyl doublets (see Tables 1 and 3). With the ' full results ' ester (Ic) ΔH° and the other thermodynamic parameters were calculated not only from the values of the areas of the bands but also from the values of their optical densities, the latter approach being the one used in many previous investigations of equilibria.[11] The energy differences so obtained (Table 1) differ considerably from those based on area measurements (Scheme), and since areas are the better measure of concentration[12] the latter are regarded as the more accurate results.]

As explained earlier, to evaluate K, and hence ΔS°, values the α_l/α_h ratio for a particular compound must be assumed to be independent of temperature. The simplest approach is to assume further that the ratio is unity: this leads to the K, ΔG°, and ΔS° values shown in the Scheme. However, it appeared preferable to attempt to measure the ratio of the α values, possibly by the approach[9] of equation (3). For this, the areas of the component bands at a given temperature must not be expressed as percentages of the total area *at this temperature*: such a procedure normalises the sum of the areas to 100% and necessarily gives $\alpha_l/\alpha_h = 1$. The component areas must be taken as percentages of the total area *at some temperature chosen to define the arbitrary 100% area*; areas at all other temperatures then correspond to this standard. Since the total areas are largest at the lowest temperatures, a consequence of ' natural decrease,' these were taken as the 100% values in the present work. Plots of A_l *versus* A_h at different temperatures gave satisfactory straight lines as judged by the correlation coefficients (Table 3). With six esters the lines had negative gradients; these gave α values, ranging from about 0·1 to 10, which were used for calculating the K', $(\Delta G^\circ)'$, and $(\Delta S^\circ)'$ figures given in Table 4. Although the absorption coefficients of corresponding cisoid and transoid forms are known to differ,[13] the wide range of α values found here is surprising. More important, with seven of the esters the lines had positive gradients: these results, which are meaningless, suggest that the method is basically unsound. The fault arises from the assumption, inherent in the approach of equation (3), that α_l (or, in a corresponding expression, α_h) is independent of temperature (*cf.* natural decrease), and the results in Table 4 are less reliable than those in the Scheme. Nevertheless the satisfactory correlation coefficients of the A_l *versus* A_h plots suggest that it should be possible to obtain true α ratios, and attempts to do so are being made.

TABLE 4

Values from attempted evaluation of α-ratios (see text)

Ester	(Ic)	(IIa)	(IIc)	(IIIc)	(IVa)	(Va)
$(\Delta S^\circ)'$	−26·4	−20·9	−12·2	18·8	6·81	13·2
$(\Delta G^\circ)'_{303}$	5490	4140	1010	−3040	−1230	−140
K'_{303}	0·088	5·3	0·67	3·3	1·6	1·1

Karabatsos *et al.*[3b] have noted that ΔH° values are unreliable when obtained from the temperature variation of n.m.r. coupling constants in a solvent whose dielectric constant (usually high) has a large temperature coefficient. Thus, dielectric constant change *per se* will influence the equilibrium proportions of rotational isomers with different dipole moments. Although this factor would be expected to be small with carbon tetrachloride solutions, investigations [the type (iii) examinations] were carried out with the object of separating the effect of a change in the dielectric constant (ε) of the solvent from that, as shown in the type (ii) runs, of changes in both dielectric constant and temperature.

---

[10] R. Mierzecki, *Acta Phys. Polon.*, 1964, **25**, 797.

[11] See discussion in ref. 12.

[12] R. A. Pethrick and E. Wyn-Jones, *Quart. Rev.*, 1969, **23**, 301.

[13] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 1960, 3425.

The idea of the present work was to simulate the effect of dielectric constant change with temperature by using appropriate solvent mixtures at constant temperature. Carbon tetrachloride and acetonitrile were chosen, since the dielectric constants of these solvents, and mixtures of them, at various temperatures have been measured accurately;[14] further, acetonitrile was not expected to favour one rotamer by preferential solvation. For three esters (Ia—c) values of A_l/A_h were measured at a fixed temperature in carbon tetrachloride–acetonitrile mixtures whose dielectric constants were found by graphical interpolation from Kalliorinne's data.[14] Treatment of the results involved the following stages. The variation of the ε values of carbon tetrachloride with temperature[14] was expressed mathematically [equation (4)]. (Regression of the ε *versus* $1/T$ plot gave a correlation coefficient of 0·996.) Equation (5) was adopted as a simple way of representing two factors (ε and T) influencing the relative band areas of the rotamers.* Combination of equations (4) and (5) led to equation (6); comparison of equations (5) and (2) gave equation (7). Plots of $\log_{10}(A_l/A_h)$ *versus* ε afforded m values for the esters. The figures for $(175{\cdot}27m + m')$ were available from the type (ii) examinations; hence m' and corrected enthalpy values, symbolised $(\Delta H^\circ)_\varepsilon$ in Table 5, were evaluated. Comparison of these with the ΔH° values (Scheme) for esters (Ia—c) shows that the dielectric variation effect is negligible for carbon tetrachloride solutions in the temperature range of the type (ii) examinations, and the effect was not investigated with the other esters.

$$\varepsilon = 175{\cdot}27(1/T) + 1{\cdot}64 \qquad (4)$$

$$\log(A_l/A_h) = m\varepsilon + m'(1/T) + \text{constant} \qquad (5)$$

$$\log(A_l/A_h) = (175{\cdot}27m + m')(1/T) + \text{constant} \qquad (6)$$

$$-\Delta H^\circ/2{\cdot}303R = m' = \{\text{observed slope } [\log(A_l/A_h) \textit{ versus } 1/T]\} - 175{\cdot}27m \qquad (7)$$

TABLE 5

Correction for dielectric constant variation by examinations (iii)

	Ester	(Ia)	(Ib)	(Ic)
Regression of $\log_{10}(A_l/A_h)$ *vs.* ε	Slope	$-0{\cdot}02$	$-0{\cdot}07$	$-0{\cdot}07$
	crc	$-0{\cdot}985$	$-0{\cdot}942$	$-0{\cdot}997$
	$(\Delta H^\circ)_\epsilon$	-959	-2140	-2710

The accuracy of the reported energy values (Scheme) is determined mainly by the magnitude of possible error in the area data, *i.e.* the stages of recording and resolving the spectra. Repeated runs with ester (Ic) led to K values within ±5% of that given here. Taking ±8% as applying generally, the statistical errors in the thermodynamic parameters were calculated by standard methods.[16]

The results will be discussed later, when the evidence for the structures of the rotamers has been presented. However, we note here that the assumption of α_l/α_h ratios of unity leads to the tentative conclusion that five of the esters exist predominantly in the thermochemically *less* stable forms at 30 °C; with these the entropy values so obtained outweigh the enthalpy differences in determining the equilibrium constants.

EXPERIMENTAL

Spectrometric.—Spectra were recorded on a Perkin-Elmer 521 spectrometer purged continuously with dry air. The instrument was operated in a linear absorbance mode (scale linear to within 1%) at a spectral slit width of 1·7 cm^{-1}, and a scanning rate of 100 cm^{-1} h^{-1}. The calibration (within 0·5 cm^{-1}) and the resolution were checked regularly against water vapour bands. For variable temperature work [examinations (ii)], cells having polytetrafluoroethylene spacers were employed with a Research and Industrial Instruments Corporation system comprising a VLT-2 probe and a TEM-1 temperature controller. Both the measurement and the control of the cell's temperature were established to be within ±0·5 °C by tests at standard temperatures. A NaCl cell (path length 0·099 cm) was used for runs in the limited range 300—340 K. The number of interference fringes between 1000 and 800 cm^{-1} from the empty cell was measured at intervals throughout this range: no change in the number (39·5 ± 0·2) was detected. Examinations over an extended range, 250—355 K, were carried out in a AgCl cell (path length 0·1121 cm). For examinations of types (i) and (iii) a range of NaCl cells of known path lengths were used. CCl_4 and MeCN were distilled from P_2O_5 and kept over molecular sieves. Solutions were made up immediately before use by weighing (to an accuracy of 0·005 mg) the solute and then, after the addition of solvent, the solution.

A DuPont Curve Resolver (model 310) fitted with an integrator was used for curve resolutions and area measurements. Errors in the precision of fit to a band contour and in area measurement were judged to be less than 4%.

Preparative.—Immediately before i.r. examination all compounds were carefully dried (and, where appropriate, distilled), and checked for purity by g.l.c. and/or t.l.c. The constants of the following compounds corresponded closely with the values in the references cited: methyl 2-furoate (Ia), b.p. 79—79·5° at 1·5 cmHg;[17] ethyl 2-furoate (Ib), b.p. 129—130° at 10 cmHg;[17] t-butyl 2-furoate (Ic), b.p. 82·5—83° at 2 cmHg;[18] methyl 3-methyl-2-furoate (IIa), b.p. 79—80° at 13 mmHg;[19] methyl 3,4-diphenyl-2-thenoate (IVa),[20] m.p. 143—144°; ethyl 3,4-diphenyl-2-thenoate (IVb),[21] m.p. 75—76°.

---

* There is no reason to expect a *linear* dependence of the equilibrium constant between rotamers on the dielectric constant of various solvent mixtures.[15] However, although the range of ε variation (2—6) in the type (iii) experiments was far greater than that (*ca.* 2·1—2·4) in the type (ii) examinations, the plots of $\log_{10}(A_l/A_h)$ *versus* ε were satisfactorily linear, thus justifying the contentious aspect of equation (6).

[14] K. Kalliorinne, *Suomen Kem.*, 1969, **42***B*, 424.

[15] R. J. Abraham and M. A. Cooper, *Chem. Comm.*, 1966, 588.

[16] E. Purlee, R. Taft, and C. De Fazio, *J. Amer. Chem. Soc.*, 1955, **77**, 837.

[17] I. Heilbron and H. Bunbury, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

[18] R. Holdren and W. Barry, *J. Amer. Chem. Soc.*, 1947, **69**, 1230.

[19] D. M. Burness, *Org. Synth.*, 1963, Coll. Vol. IV, p. 649.

[20] J. L. Melles and H. J. Bacher, *Rec. Trav. chim.*, 1953, **72**, 314.

[21] H. Wynberg and H. J. Kooreman, *J. Amer. Chem. Soc.*, 1965, **87**, 1739.

Ethyl 3-*Methyl*-2-*furoate* (IIb).—A solution of 3-methyl-2-furoic acid [22] (282 mg) in dry EtOH (12 ml)–H_2SO_4 (1 ml) was refluxed for 3 h. Work-up followed by distillation gave the *ethyl ester* (205 mg), b.p. 100—105° (bath temp.) at 1 cmHg, which slowly crystallised (Found: C, 62·35; H, 6·55. $C_8H_{10}O_3$ requires C, 62·65; H, 6·8%), τ 5·71 (q, *J* 7·0 Hz, OEt), *m*/*e* 154 (M^+, 37%).

t-*Butyl* 3-*Methyl*-2-*furoate* (IIc).—Isobutene (10 ml) was added to a suspension of 3-methyl-2-furoic acid [22] (1 g) in dry Et_2O (80 ml)–H_2SO_4 (2 ml) which was contained in a thick-walled vessel fitted with a magnetic stirrer and cooled to −40 °C. A tightly fitting stopper was wired on to the vessel, the cooling mixture was removed, and the mixture was stirred at 20 °C for 3 days, cooled, and poured carefully into KOH (6 g)–H_2O (150 ml) at 0 °C. Work-up gave the *t-butyl ester* (0·53 g), b.p. 55—60° (bath temp.) at 0·05 mmHg, n_D^{19} 1·4755 (Found: C, 66·2; H, 7·75. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%), τ 8·44 (s, Bu^t), *m*/*e* 183 (M^+, 41%).

We thank the S.R.C. for grants (to D. J. C., J. C., and R. L. S.).

[2/496 *Received*, 3*rd March*, 1972]

---

[22] D. M. Burness, *Org. Synth.*, 1963, Coll. Vol. IV, p. 628.