Enthalpy and Entropy Differences between the Forms of Simple Heterocyclic Aldehydes in Carbon Tetrachloride Solution

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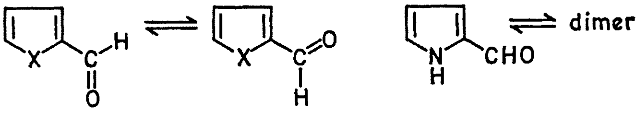
Summary The enthalpy and entropy changes for the internal rotation of furan- and thiophen-2-aldehydes, and for the dimerisation of pyrrole-2-aldehyde have been determined.

MANY examples of internal rotation have been detected by i.r. spectrometry (notably the observation of twin carbonyl peaks for compounds containing only one carbonyl group)[1] but surprisingly little quantitative work has been reported, and the proportions of rotational isomers have been evaluated more frequently by n.m.r. spectrometry.[2] Where energy differences rather than energy barriers are to be examined, certain advantages (accuracy of quantitative measurement, unambiguity of interpretation) accrue from the use of the i.r. rather than the n.m.r. method. I.r. spectrometry is well suited to the present study of the equilibria between the various forms of furan- , thiophen- , and pyrrole-2-aldehydes in carbon tetrachloride solution. Furfural gives twin carbonyl peaks;[3] these are generally attributed to rotational isomers[4] although a different explanation has been advanced.[5] With pyrrole-2-aldehyde the doublet is known to arise from a monomer–dimer equilibrium.[6] The published spectrum of thiophen-2-aldehyde[7] did not show a split carbonyl peak.

Dry solutions of the three aldehydes in carbon tetrachloride were examined from 1750 to 1600 cm^{-1} on a high resolution spectrometer (spectral slit-width 1·7 cm^{-1}) purged continuously with dry air, (i) at different concentrations and constant temperature (288°K), (ii) at a fixed initial concentration over the range 258—348°K, and (iii) at constant concentration and temperature (288°K) but with the solvent containing increasing amounts of acetonitrile. Analysis of the spectra with a Dupont 310 resolver gave components having about 70% Lorentzian character. In all cases the analysis led to two main bands (constituting over 91% of the total absorption) and minor peaks (one for furfural, two for the other aldehydes) which are not further discussed here. The characteristics of the main bands of furfural are shown in the Table: results for the other compounds[8] will be given in the full publication.



(1a),(2a) (1b),(2b) (3a) (3b)

X	ν_{max} (cm^{-1})	ΔH^0 ($J mol^{-1}$)	ΔS^0 ($J °K^{-1} mol^{-1}$)
O	(**1a**) (1700) ⇌ (**1b**) (1681)	−3198 ± 297	−18·21 ± 2·01
S	(**2a**) (1688) ⇌ (**2b**) (1677)	−7409 ± 301	−37·38 ± 4·02
NH	(**3a**) (1664) ⇌ (**3b**) (1654)	−29,511 ± 402	−63·6 ± 2·68

Results for furfural†

Expts. (i)	A(**1b**)/A(**1a**)	0·399	0·399	0·399	0·409	0·389
	Concn. (g/l)	8·59	1·72	0·86	0·43	0·090
Expts. (iii)	A (**1b**)/A (**1a**)	0·408	0·667	0·709	0·754	0·786
	Dielectric constant	2·25	3·00	3·50	4·00	4·66

Expts. (ii)	Temp. (°K)	D (**1a**)	D (**1b**)	log[A (**1b**)/A (**1a**)]	ΔG^0 ($J mol^{-1}$)
	253	0·54	0·26	−0·278	1343
	263	0·54	0·24	−0·308	1547
	277	0·54	0·23	−0·327	1729
	283	0·54	0·22	−0·348	1880
	293	0·54	0·20	−0·400	2238
	303	0·53	0·18	−0·421	2435
	313	0·52	0·17	−0·432	2581
	323	0·52	0·16	−0·443	2731
	333	0·51	0·15	−0·454	2886
	343	0·50	0·14	−0·466	3052

The results of experiments (i) established conclusively that form (**3b**) is a dimer, and excluded the operation of intermolecular association with the other two aldehydes. In handling the results of experiments (ii), two rather subtle features must be recognised. With several normal ketones which we have examined (*e.g.*, 5α-androstan-3-one) heating the solution causes the C=O band to decrease in intensity (whether expressed in terms of optical density or of area). This "natural decrease," of which only about one half can be attributed to expansion of the solution, parallels the behaviour of certain aromatic compounds:[9] the use of area ratios in the present work circumvents this difficulty. Further, as the temperature varies so does the dielectric constant of carbon tetrachloride, and the dielectric constant change *per se* will affect the intensity ratio.[5] The change

† A refers to the % area and D to the optical density of a band; *e.g.* A(**1b**) = [area of band (**1b**)]100/[total area of bands (**1a**) + (**1b**)].

in dielectric constant with temperature can be obtained from Kalliorinne's work,[10] and the object of experiments (iii) was to simulate this effect at constant temperature for furan- and thiophen-2-aldehydes. (With pyrroles the situation is different in that the effects of changing solvent arise from local interactions[11] rather than from the variation in dielectric.) Treatment of the data by linear regression analysis gave good correlation coefficients, and the effect of temperature variation alone on the equilibria was extracted from the results.[7] ΔH° values were then calculated, and an adaptation of a recent method[11] was used in obtaining ΔS° figures: the precision of the values was assessed by the procedure of ref. 12.

Correlations between particular rotamers and the forms of the aldehydes cannot be made unequivocally; definitive work on this problem is in progress. In carbon tetrachloride solution at 20° furfural exists mainly in the thermochemically less stable form (**1a**). We are inclined to correlate this form with the cisoid-structure (see Table), an assignment which appears to agree with dipole moment studies[14] and with the n.m.r. work[15] which gave ΔH° $-4{\cdot}40 \pm 0{\cdot}21$ kJmol^{-1} and ΔS^0 $-9{\cdot}08 \pm 0{\cdot}75$ J°K^{-1}mol^{-1}. At 20° the equilibrium constant for furfural ([**1b**]/[**1a**]) is 0·399: although ΔH^0 is numerically larger with thiophen-2-aldehyde there is a relatively greater increase in ΔS^0 and the equilibrium constant ([**2b**]/[**2a**]) decreases to 0·245. The more pronounced mesomerism in pyrrole-2-aldehyde leads to a monomer with appreciable charge separation: the tendency for dimerisation is thereby enhanced, and the dimer may be further stabilised by intermolecular hydrogen bonding.

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