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EMPIRICAL DETERMINATION OF MEDIUM EFFECTS ON THE EQUILIBRIUM BETWEEN *trans cis* AND *trans trans* 1,2-DIBROMO-4-t-BUTYLCYCLOHEXANES

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Summary. Head space analysis, GLC retention time data, and solution calorimetry are used to determine the effect of medium on the thermodynamic parameters for the equilibrium (1)$\rightleftharpoons$(2). It is shown that changes in ΔG^o and ΔH^o can be evaluated for the transfer of the equilibrium from a series of solvents to the gaseous phase which is used as the reference medium.

Conformational equilibria within compounds containing vicinal halogen atoms have attracted much attention and have been used for testing solvation theories.[1,2] Such theories stand or fall on the degree of correlation between calculated data and experimental values. The latter are obtained by assorted physical methods which, though suitable for the solution phase, are seldom appropriate for the vapour state. Indeed, data for this state, which provides a useful reference medium, are invariably scarce. The present work concerns the dibromocompounds (1) and (2). Although the equilibrium between (1) and (2) is infinitely slow at room temperature it can be defined, nevertheless, in terms of ΔG^o and ΔH^o. We show that relatively simple techniques can be used to obtain the variation in these thermodynamic parameters over a range of media which includes not only solvents but also the vapour phase.

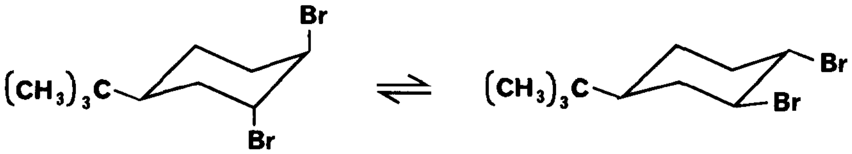

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Table 1

Values of $\delta\Delta G^o$ (gas phase → solvent) for the equilibrium $(1) \rightleftharpoons (2)$ at 298 K obtained using the Headspace Analysis Method[a]

Solvent:	Squalane	Cyclohexane	CCl_4	Benzene	Acetone
$[\frac{([1]/[2])_g}{([1]/[2])_s}]$:	2.42	1.90	1.79	4.79	5.30
$\delta\Delta G^o_{g\to s}$/K cal mol^{-1}:	-0.51[b]	-0.38	-0.34	-0.92	-0.99

[a] Errors in $\delta\Delta G^o_{g\to s}$ average ± 0.05 K cal mol^{-1}. [b] Compare the value of -0.52 obtained by the retention time method, Table 2.

Table 2

Values of $\delta\Delta G^o$, $\delta\Delta H^o$, and $\delta\Delta S^o$, (gas phase→squalane and di-isodecylphthalate) for $(1) \rightleftharpoons (2)$ obtained using the GLC Retention Time Method

	T K	$\delta\Delta G^o_{g\to s}$ K cal mol^{-1}	$\delta\Delta H^o_{g\to s}$ K cal mol^{-1}	$\delta\Delta S^o_{g\to s}$ cal K^{-1} mol^{-1}
Gas phase →Squalane[a]	409.7	-0.36	-1.50	-2.8
	399.4	-0.39	-1.42	-2.6
	388.1	-0.42	-1.33	-2.3
	379.5	-0.44	-1.26	-2.2
	369.5	-0.46	-1.18	-1.9
	359.5	-0.47	-1.09	-1.7
	349.7	-0.49	-1.00	-1.5
	298.2[b]	-0.52	-0.41	+0.4
Gas phase → Di-isodecylphthalate[c]	365.1	-0.45	-1.36	-2.5
	355.0	-0.48	-1.36	-2.5
	344.0	-0.51	-1.36	-2.5
	336.0	-0.52	-1.36	-2.5
	298.2[b]	-0.62	-1.36	-2.5

[a] With 3% squalane on celite as the GLC stationary phase.

[b] Extrapolated value.

[c] With 5% di-isodecylphthalate on celite as the GLC stationary phase.

The principal technique utilises gas chromatographic head-space analysis and involves measuring the composition of the vapours in the head-space above a solution containing a known ratio of (1) and (2) in a solvent s. Previously we used this method for measuring the variation in ΔG^o with solvent, i.e. $\delta\Delta G^{o}_{s\rightarrow s'}$, for the cis and trans 4-t-butylcyclohexanol equilibrium,[3] but here we treat the results for $(1)\rightleftharpoons(2)$ via equation I to give the difference in ΔG^{o} in the gas phase and solution, i.e. $\delta\Delta G^{o}_{g\rightarrow s}$. Results are given in Table 1.

$$\delta\Delta G^{o}_{g\rightarrow s} = -RT\ln\left[\frac{([1]/[2])_g}{([1]/[2])_g}\right] \qquad (I)$$

In principle, it would be possible to obtain $\delta\Delta H^{o}_{g\rightarrow s}$ by the temperature variation of $\delta\Delta G^{o}_{g\rightarrow s}$ using the head-space analysis, but the method is not yet sufficiently accurate. We therefore measured $\delta\Delta G^{o}_{g\rightarrow s}$ by the GLC retention time method,[4] using squalane and di-isodecylphthalate as the stationary liquid phases, through equation II where t_1 and t_2 are

$$\delta\Delta G^{o}_{g\rightarrow s} = -RT\ln(t_2/t_1) \qquad (II)$$

the retention times of isomers (1) and (2). This method is accurate enough to obtain $\delta\Delta H^{o}_{g\rightarrow s}$ values from the temperature variation of $\delta\Delta G^{o}_{g\rightarrow s}$, although extrapolation from higher temperatures to 298 K is necessary. Results are reported in Table 2 and show, quite surprisingly, that $\delta\Delta H^{o}$ for the gas → squalane transfer varies markedly with temperature.

Table 3

Values of $\delta\Delta H^{o}$, $\delta\Delta G^{o}$ and $\delta\Delta S^{o}$ (gas phase → solvent) for the equilibrium $(1)\rightleftharpoons(2)$ at 298 K[a]

	$\Delta H^{o}_{s}(1)$	$\Delta H^{o}_{s}(2)$	$\delta\Delta H^{o}_{g\rightarrow s}$	$\delta\Delta G^{o}_{g\rightarrow s}$	$\delta\Delta S^{o}_{g\rightarrow s}$
Gas phase	-	-	0	0	0
Di-isodecylphthalate	0.16[b]	-0.09[b]	-1.36[d]	-0.62[d]	-2.5
Squalane	0.34[b]	0.75[b]	-0.70[e]	-0.52[d]	-0.6
Cyclohexane	0.53[c]	1.27[c]	-0.37	-0.38[f]	0.0
CCl_4	-0.19[c]	0.38[c]	-0.56	-0.34[f]	-0.7
Benzene	0.52[c]	-0.08[c]	-1.71	-0.92[f]	-2.6
Acetone	1.46[c]	0.83[c]	-1.74	-0.99[f]	-2.5

[a] Enthalpy and free energy terms in K cal mol^{-1}, entropy in cal K^{-1} mol^{-1}. Errors in ΔH^{o}_{s} are ±0.02 K cal mol^{-1} for present work and ±0.03 in data from ref. 6. Errors average ±0.05 K cal mol^{-1} in $\delta\Delta G^{o}_{g\rightarrow s}$, ±0.2 K cal mol^{-1} in $\delta\Delta H^{o}_{g\rightarrow s}$ and ±0.7 cal K^{-1} mol^{-1} in $\delta\Delta S^{o}_{g\rightarrow s}$. [b] Enthalpy of solution by direct calorimetry, this work. [c] As b, data from ref. 6. [d] Values from Table 2. [e] From $\delta\Delta H^{o}$ (gas → di-isodecylphthalate) = -1.36 and $\delta\Delta H^{o}$ (squalane → di-isodecylphalate) = -0.66 K cal mol^{-1}. [f] Values from Table 1.

Reisse et al [5,6] have shown that measurement of enthalpies of solution of separate isomers such as (1) and (2) in a series of solvents yields accurate and reliable values of $\delta\Delta H^{o}$ between one solvent and another, i.e. $\delta\Delta H^{o}_{s\rightarrow s'}$. We can extend Reisse's data [6] for (1)⇌(2) by the measurement of enthalpies of solution of (1) and (2) in squalane and in di-isodecylphthalate, and then by use of the known values (Table 2) of $\delta\Delta H^{o}_{s\rightarrow s}$ for these two solvents we can refer all the enthalpy data to the gas phase. We find by direct calorimetry (Table 3) that $\delta\Delta H^{o}$ (squalane→di-isodecylphthalate) = -0.66 ± 0.04 K cal mol^{-1}, cf -0.95 ± 0.4 K cal mol^{-1} obtained by the GLC retention time method, (-1.36 + 0.41), Table 2. The values are in satisfactory agreement and within the experimental errors which arise mainly in extrapolating the Van't Hoff plots. We take -0.66 K cal mol^{-1} as the correct difference and use the value for $\delta\Delta H^{o}_{g\rightarrow s}$ for di-isodecylphthalate to obtain the remaining $\delta\Delta H^{o}_{g\rightarrow s}$ data in Table 3.

We are at present extending the head-space analysis method to a wider range of solvents and reserve discussion of results until this aim is achieved. However, it is already clear from data in Table 3 that for the equilibrium (1)⇌(2), inert solvents such as cyclohexane are fairly good models for the gas phase.

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