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A SOLVENT INDUCED BAKER-NATHAN ORDER IN A NON-REACTING SYSTEM

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There has been a great deal of interest in the Baker-Nathan order and a long lived controversy over its source continues.[1] We wish to report the observation of significant (nearly 1 kcal/mole) Baker-Nathan orders resulting from the transfer of a series of monoalkyl benzenes from carbon-tetrachloride to a series of solvents of higher cohesive energy density.[2] This is a Baker-Nathan order induced by changes in non-specific solvation[3] of relatively non-polar molecules. This effect will be important whenever thermodynamic measurements are made involving the transfer of a molecule between two solvents. This has been the case often in studies of the Baker-Nathan order.[4] There will also be a smaller contribution whenever there is a change in the size of the molecule on passing from the ground state to the transition state. The importance of this internal pressure effect on the conformation of some silapentanes has been discussed quite recently by Ouellette and Williams.[5]

The heat of transfer of an organic solute from one solvent to another may be considered to be the sum of several different interactions. Using a treatment similar to Friedman's,[6] we shall split the heat of transfer into contributions due to van der Waal's interactions (ΔH_w), specific solute-solvent interactions (ΔH_s) such as hydrogen bond formation, and a contribution due to the formation of a cavity in the solvent to contain the solute (ΔH_c). The effects of solvent structure are felt to be very small in most non-protic organic solvents and can be safely ignored.

Of the three factors defined above, we find that the cavity term (ΔH_c) is dominant in causing the differences in heats of transfer of the monoalkyl benzenes as the alkyl group is varied (Me, Et, iPr, and *t*-Br). The data are given in Table 1. Alkylbenzenes are known to form weak complexes with carbon tetrachloride[7] and a variety of other materials.[7,8] However, the substitutent effects on the stability of these complexes are much too small to explain the data reported here.[8,9,10] Arnett has recently investigated the heats of transfer of a series of amines and alcohols from carbon-tetrachloride to fluorosulfonic acid and concluded that the London dispersion interactions were quite similar in these two very different solvents.[11] Data presented by Friedman[6] also indicate the effects of varying solvent on these interactions will be small. In any event, such interactions are expected to result in increasing stability with increasing size of the alkyl group as the dipole moment of the solvent increases. This is contrary to the data presented in Table 1.

In the absence of any specific interactions the energy required to create a cavity in a solvent will increase with the size of the solute molecule. As it becomes harder to create the cavity, the difference in energy between toluene and t-butylbenzene will increase. We can use the solubility perameter[2] ($\delta = (\frac{\Delta Ev}{Vl})^{1/2}$) as an index of the energy required to create a cavity in the solvent. Two predictions can be made: (1) In the absence of any specific interactions, the heat of transfer of a single solute from carbon tetrachloride to another solvent will become increasingly endothermic as the cohesive energy density for the second solvent increases.[12] (2) There should be an increasing difference between the heats of transfer along the series of alkylbenzenes as δ for the second solvent increases. For example, the heat of transfer of the t-butyl compound will become increasingly endothermic when compared with the heat of transfer of the methyl substituted compound. This second effect will be independent of specific solute-solvent interactions since these are expected to be essentially identical for a series of mono-alkyl benzenes.[8,9,10,13]

An examination of the data in Table 1 shows that the first prediction is followed well, but not perfectly. The alkyl benzenes show general agreement with it, although there are exceptions when going from carbon tetrachloride to methylene chloride. If the other solvents are used to establish a series, carbon tetrachloride is exceptional. The agreement is surprisingly good considering the crude nature of the approach.

The second prediction is followed very well in all solvents but carbon tetrachloride, and the effects can be quite large. For example, the difference between the heats of transfer of toluene and t-butylbenzene from carbon tetrachloride to nitromethane is 0.74 kcal/mole. For the carbon tetrachloride 1,2-dibromoethane pair, the difference is 0.43 kcal/mole. These effects are larger than most of the Baker-Nathan orders observed in solvolysis reactions.[1]

This effect is in the same order as the substituent effect on the heats of protonation observed by Arnett and Larsen;[4c] However, it is too small to explain their data, and other

Table 1. Heats of Solution (kcal/mole) of Alkylbenzenes ($R-C_6H_5$) in a Series of Solvents at 25°[a]

Solute (δ)	CCl_4[b] (8.6)	CH_2Cl_2 (9.7)	Dioxane (10.0)	$BrCH_2CH_2Br$ (10.4)	CH_3NO_2 (12.6)	$H_3C\overset{O}{\overset{\|}{S}}CH_3$[c]	$H_3C-\overline{CH-CH_2-O-COO}$[c]
R							
H (9.15)	+0.15±.02	-0.46±.01	+0.06±.01	+0.30±.04	+1.15±.02	+0.63	+0.37
Me (8.90)	-0.09±.04	-0.10±.03	+0.21±.02	+0.24±.02	+1.23±.02	+0.90	+0.56
Et (8.80)	+0.13±.04	+0.07±.04	+0.39±.02	+0.45±.04	+1.63±.02	+1.12	+0.76
i-Pr (8.53)	+0.21±.06	+0.14±.02	+0.51±.02	+0.62±.04	+1.75±.02	+1.36	+0.89
t-Bu (8.35)	-0.08±.03	+0.19±.04	+0.58±.03	+0.68±.03	+1.98±.02		

a) The calorimeter and procedures used have been described before (ref. 4d). All values reported are the average of at least 6 independent measurements and the errors are standard deviations.

b) Data from ref. 4c.

c) Data from ref. 6.

effect(s) must be operating. The data presented here indicate that the effect of solvent cohesive energy density on heats of transfer is significant and can generate a Baker-Nathan order. But this effect is not large enough to explain the large Baker-Nathan orders recently observed with stable cations.[4c,d,e] A more quantitative discussion of these interactions will be presented in a full paper.

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12. This is not necessarily so if regular solution theory is used. With this model the heat of transfer of C from A to B is given by $\Delta H_T = V_C(\delta_A-\delta_B)(\delta_A+\delta_B-2\delta_C)$ and is a function not only of the solvents and volume of the solute, but also of δ for the solute. The data presented here do not agree well with predictions based on regular solution theory. The use of various quantitative models for calculating solvent effects on ground states will be explored in a full paper.
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