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NEMATIC–ISOTROPIC SOLUTION THERMODYNAMICS IN DI(*p*-METHOXYPHENYL)-*trans*-CYCLOHEXANE-1,4-DICARBOXYLATE

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ABSTRACT

Solution thermodynamic parameters of selected non-polar solutes have been determined in the nematic and isotropic fluid states of di(*p*-methoxyphenyl)-*trans*-cyclohexane-1,4-dicarboxylate. These states have been reported to exert no measurable differential in kinetic medium effects on the Claisen rearrangement[1]. Partial molar enthalpies $\Delta\bar{H}_2^{\text{soln}}$ and entropies $\Delta\bar{S}_2^{\text{soln}}$ of solution of a series of substituted benzenes in the nematogenic solvent, determined by the gas–liquid chromatographic method of Martire, et al.[2–4], are reported. Changes in solute excess Gibbs free energy $\Delta\bar{G}_2^{\text{E}}$ over the nematic–isotropic transition of the solvent, corresponding to the changes in free energy of solution $\Delta\Delta\bar{G}_2^{\text{soln}}$, have been calculated for the series. The results show the nematic and isotropic states of the medium to exhibit distinctly different solvent characteristics and suggest that Claisen reaction kinetics in the nematogenic solvent reflect compensating medium effects on the reactant and its activated state.

INTRODUCTION

The activation enthalpy $\Delta H^{\ddagger}$ and activation entropy $\Delta S^{\ddagger}$ of the Claisen rearrangement of a series of *para*-substituted allyl phenyl ethers have been reported to be insensitive to the transition of the solvent, di(*p*-methoxyphenyl)-*trans*-cyclohexane-1,4-dicarboxylate (DMCD), from its nematic to its isotropic form[1]. These observations are in contrast to discontinuities which have been observed in the thermodynamic parameters of various non-polar solutes in several thermotropic liquid crystalline solvents at the transition temperatures to and from their various anisotropic fluid states[2,3]. Because of the extended temperature range, 143–242°C, over which DMCD exists as a nematic liquid[5], it is attractive as a liquid crystalline medium in which to study solute chemical behavior in general and isokinetic or isoequilibrium relationships in particular. The present work provides information regarding the comparative medium effects of the molecular order of DMCD in the solution thermodynamics of selected non-polar solutes.

EXPERIMENTAL

A Perkin-Elmer gas chromatograph, Model 900, equipped for flame ionization detection, was used to determine solute specific retention volumes against methane as the reference. Johns-Manville 60–80 mesh, acid washed Chromosorb P was coated with DMCD using methylene chloride as a solvent. After natural evaporation of the solvent at room temperature, 12 g of the coated solid support (containing 14.6% by weight of DMCD) were packed into a 120-cm length of 6.35 mm ID copper tubing. The column was conditioned at 160°C with a moderate flow of nitrogen carrier gas for 24 h prior to use. The injection chamber was held at a temperature of 275°C and the manifold at 300°C throughout the studies. For the higher temperature measurements, the column was re-equilibrated until a satisfactory baseline was attained. Temperatures were held to within ±0.25°C by the standard oven controls. Carrier gas inlet pressure was measured with a Perkin-Elmer gauge and was adjusted to give suitable elution times and column efficiencies. Flow-rates were determined at the outlet with a soap-film meter and detector responses were recorded with a 1-mV Honeywell "Electronic" 194 recorder at a chart speed of 25.4 mm min^{-1}. Solute samples were injected using a 1-μl Hamilton syringe and ranged in volume from 0.1 to 0.2 μl. Retention times, taken as the average of four to five measurements, were determined for each solute at ten temperatures spaced over the interval from 150 to 275°C.

The liquid crystalline compound, DMCD, was prepared by reacting *trans*-cyclohexane-1,4-dicarboxylic acid successively with thionyl chloride and *p*-methoxyphenol[5]. The resultant nematogenic compound was recrystallized twice from aqueous alcohol and its identity and purity verified by ultraviolet, infrared, nuclear magnetic resonance and mass spectroscopy. Solid–nematic and nematic–isotropic transition temperatures were determined, using a Bausch and Lomb polarizing microscope fitted with a Kofler hot stage, and found to be 143 and 242°C, respectively, in agreement with previously reported values[5].

Volatile solutes selected for study were: benzene (Fisher Scientific Co.); toluene (J. T. Baker Chemical Co.); ethylbenzene (Aldrich Chemical Co.); n-propylbenzene, *o*-xylene, *m*-xylene and *p*-xylene (Eastman Kodak Co.). With the exception of the xylenes which were used as received, the solutes were distilled and only the middle 40% fraction was used. No detectable impurities were apparent in the chromatograms.

RESULTS AND DISCUSSION

No tailing, peak skewness or changes in retention time with sample size were noted in the course of the experimentation, confirming operation within the Henry's law concentration range. However, other secondary effects arising from interactions of the solid support with the nematogenic solvent and with the volatile solutes could detract from the validity of the results.

In a recent review[6], Saupe discusses the disclinations which are known to occur in nematic liquids and which are manifested as singular and non-singular lines and as singular points. Such disclinations can easily be produced experimentally by certain boundary conditions such as capillaries, sharp points and edges or other small scale irregularities as might be found on the surface of gas chromatographic solid supports. While the textures of bulk nematic liquids normally reveal the presence of disclinations, the induction of an unusually high density of such discontinuities could result in altered solvent characteristics. In addition to these effects, adsorption with the presence of Gibbs excess concentrations of solute at the solid–liquid and gas–liquid interfaces must be considered. Possible deviations from bulk behavior due to these causes have been investigated by Chow and Martire[4] but were found to be negligible under the conditions of experimentation as reported in the present work.

Retention times of the solutes, t, and of methane, t_0, were used to calculate the specific retention volumes V_g° from the relationship[7]

$$V_g^\circ = f(t-t_0)\,F/w \tag{1}$$

where f is a correction factor for the pressure drop across the column, F is the flow-rate and w is the weight of the stationary liquid. Infinite dilution solute activity coefficients γ_p^∞ were calculated from the equation[8]

$$\gamma_p^\infty = \frac{1.704\times 10^7}{M p_2^\circ V_g^\circ} \tag{2}$$

where M and p_2° are the solvent molecular weight (384.4) and the calculated vapor pressure[9,10] of the pure solute, respectively.

Second virial coefficients of the pure solute vapor, B_{22}, calculated from a modified equation of corresponding states[11–13], with literature values of the necessary critical constants[10,14], were used to correct the infinite dilution activity coefficients for vapor phase non-ideality by means of the following expression[15]:

$$\ln \gamma_f^\infty = \ln \gamma_p^\infty - \frac{p_2^\circ B_{22}}{RT} \tag{3}$$

Activity coefficients obtained by this method have been shown to agree favorably with those obtained from classical static measurements[16].

The solute partial molar excess free energy, $\bar{G}_2^E$, enthalpy, $\bar{H}_2^E$, and entropy, $\bar{S}_2^E$, at infinite dilution are related to γ_f^∞ by the following relationship from solution thermodynamics[17]:

$$RT\ln \gamma_f^\infty = \bar{G}_2^E = \bar{H}_2^E - T\bar{S}_2^E \tag{4}$$

The excess enthalpies and entropies, presented in Table 1, were obtained from the slopes and intercepts of linear least-square regression curves of $\ln \gamma_f^\infty$ vs. T^{-1}. From eqn (4), these slopes and intercepts are seen to equal $\bar{H}_2^E/R$ and $-\bar{S}_2^E/R$, respectively. These values of $\bar{H}_2^E$ and $\bar{S}_2^E$ are comprised of contributions from solvent–solvent, solvent–solute and solute–solute interactions. For the purpose of comparison of relative solvent–solute interaction enthalpies and entropies among solutes, it is sufficient

TABLE 1

PARTIAL MOLAR EXCESS PROPERTIES OF SOLUTES IN DMCD

Enthalpies are in kcal mol^{-1} and entropies are in cal deg^{-1} mol^{-1}; probable errors are in the same units, respectively.

Solute	*Nematic*		*Isotropic*	
	$\bar{H}_2^E$	$\bar{S}_2^E$	$\bar{H}_2^E$	$\bar{S}_2^E$
Benzene	3.63 ± 0.20	8.82 ± 0.44	4.04 ± 0.18	8.96 ± 0.34
Toluene	4.25 ± 0.23	9.77 ± 0.50	4.38 ± 0.57	8.87 ± 1.04
Ethylbenzene	4.86 ± 0.27	10.63 ± 0.60	4.42 ± 0.20	8.36 ± 0.37
Propylbenzene	5.37 ± 0.30	11.34 ± 0.66	4.70 ± 0.37	8.28 ± 0.74
o-Xylene	4.74 ± 0.27	10.51 ± 0.59	5.17 ± 0.83	9.56 ± 1.53
m-Xylene	4.67 ± 0.28	10.26 ± 0.62	6.06 ± 0.12	11.24 ± 0.21
p-Xylene	4.15 ± 0.23	9.23 ± 0.58	5.49 ± 2.08	10.27 ± 2.60

to correct for solute–solute contributions since solvent–solvent terms will be constant in a given phase of DMCD. This can be accomplished to a close approximation by subtracting the heats and entropies of vaporization according to the following expressions[2]:

$$\Delta\bar{H}_2^{\text{soln}} = \bar{H}_2^E - \Delta H_2^{\text{vap}} \tag{5}$$

$$\Delta\bar{S}_2^{\text{soln}} = \bar{S}_2^E - \Delta H_2^{\text{vap}}/T \tag{6}$$

Values of the partial molar enthalpies and entropies of solution, calculated from eqns (5) and (6) using heats of vaporization, ΔH_2^{vap}, derived from Dreisbach's data[9,10], are reported in Table 2. A linear relation was found between the enthalpies and entropies of solution of the benzene and xylene series. The least-square slopes β and correlation coefficients, r, for this relationship are shown in Table 3. Criteria for

TABLE 2

PARTIAL MOLAR ENTHALPIES AND ENTROPIES OF SOLUTION IN DMCD

Enthalpies are in kcal mol^{-1} and entropies are in cal deg^{-1} mol^{-1}. For computation, average experimental temperatures were taken as 160 and 260 °C in the nematic and isotropic phases, respectively.

Solute	*Nematic*		*Isotropic*	
	$-\Delta\bar{H}_2^{\text{soln}}$	$-\Delta\bar{S}_2^{\text{soln}}$	$-\Delta\bar{H}_2^{\text{soln}}$	$-\Delta\bar{S}_2^{\text{soln}}$
Benzene	2.21	4.66	1.55	1.53
Toluene	2.51	5.84	2.16	3.41
Ethylbenzene	2.71	6.82	2.97	5.51
Propylbenzene	2.93	7.83	3.48	7.06
o-Xylene	2.70	6.67	2.04	3.96
m-Xylene	2.98	7.41	1.44	2.82
p-Xylene	3.48	8.39	1.98	3.73

TABLE 3

SLOPES AND CORRELATION COEFFICIENTS OF $\Delta\bar{H}_2^{\mathrm{soln}}$ vs. $\Delta\bar{S}_2^{\mathrm{soln}}$

Solute	*Nematic*		*Isotropic*	
	β *(K)*	*r*	β *(K)*	*r*
Benzene series	224	0.999	355	0.999
Xylene series	454	0.997	558	0.995

evaluating the significance of such apparent isoequilibrium relationships have been discussed by Leffler[18]. Data for the benzene series are plotted in Fig. 1 and meet Leffler's suggested requirements for a good r value coupled with a significant range in both enthalpy and entropy relative to their precision. The slopes of the probable error lines and the least-square regression lines in Fig. 1 are equal to the mean experimental temperatures $\bar{T}_{\mathrm{exp}}$ and the isoequilibrium temperatures, β, respectively. It should be noted that the values of $\bar{T}_{\mathrm{exp}} - \beta$ are exceptionally large; 209 °C for the nematic and 178 °C for the isotropic state.

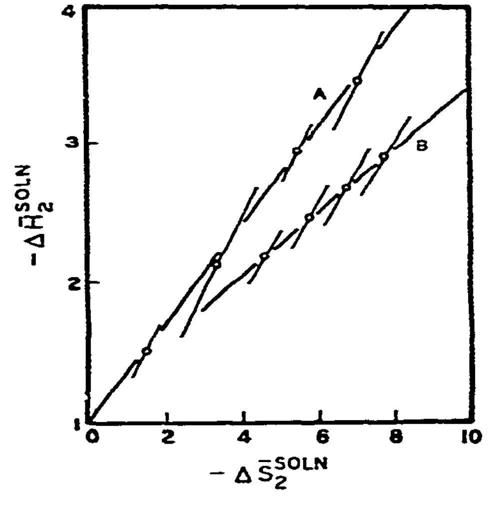

Fig. 1. Entropy–enthalpy of solution correlation plot. Entropies and enthalpies of solution are expressed in units of cal deg^{-1} mol^{-1} and kcal mol^{-1}, respectively, in the isotropic (A) and nematic (B) phases of DMCD. Substituents for the series of substituted benzenes are, from left to right: –H, $-CH_3$, $-CH_2-CH_3$, $-CH_2-CH_2-CH_3$.

Although, in the case of the xylene series, experimental precision is insufficient to support the existence of an isoequilibrium relationship, a discontinuity in thermodynamic behavior over the transition temperature similar to that shown in Fig. 1, is readily apparent. This discontinuity can be expressed quantitatively by the change in the excess Gibbs free energy of the solutes, $\Delta\bar{G}_2^{\mathrm{E}}$, as the solvent passes from the nematic to the isotropic state. Since $\Delta\bar{G}_2^{\mathrm{E}}$ equals the change in free energy of solution,

$\Delta\Delta\bar{G}_2^{\text{soln}}$, this is equivalent to comparing changes in solubility characteristics neglecting solute–solute interactions. Values of $\Delta\Delta\bar{G}_2^{\text{soln}}$ at 242 °C, calculated from the transition temperature intercepts of linear least-square regression curves of ln γ_f^{∞} vs. T^{-1}, from eqn (4), are presented in Table 4 and show a general increase with increasing chain-length.

TABLE 4

SOLUTE NEMATIC–ISOTROPIC TRANSITION $\Delta\Delta\bar{G}_2^{\text{soln}}$ ($\Delta\bar{G}_2^{E}$) IN DMCD

Correlation coefficients, *r*, correspond to linear least-square regression curves of ln γ_f^{∞} vs. T^{-1} which were extrapolated to the transition temperature of 515 K.

Solute	$\Delta\Delta\bar{G}_2^{\text{soln}}$ (*cal mol*$^{-1}$)	*Correlation coefficients, r*	
		Nematic	*Isotropic*
Benzene	346	0.983	0.998
Toluene	593	0.984	0.981
Ethylbenzene	734	0.983	0.998
Propylbenzene	907	0.983	0.993
o-Xylene	924	0.983	0.972
m-Xylene	893	0.980	0.999
p-Xylene	802	0.979	0.875

The results obtained in the present study demonstrate some differences that can be expected in the solution thermodynamics of certain solutes in the fluid states of DMCD. The lack of an observable nematic–isotropic medium effect by this solvent on the Claisen rearrangement, as reported by Bacon and Brown, is not due to a lack of a significant change in its solvent properties.

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