

The Measurement of Transfer Enthalpy in Mixed Solvent (Part 2) Solvent Effects on Nucleophilic Substitution Reactions of Ethyl and 2-Phenylethyl Benzenesulfonates

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Heats of solution of aniline (AN), benzylamine (BA), ethyl-(EBS) and 2-phenylethyl benzenesulfonates (PEB) are calorimetrically measured in acetonitrile-methanol mixtures at 25.0 °C. The activation parameters, ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger , are determined for the reactions of EBS and PEB with AN and BA using the kinetic data at three temperatures. Calorimetric transfer enthalpies of initial state, $\delta H_i^{\circ\ddagger}$ (IS), and kinetically derived activation enthalpies, $\delta \Delta H^\ddagger$, in the MeCN-MeOH mixtures are combined to determine the transfer enthalpies of transition state, $\delta H_i^{\circ\ddagger}$ (TS);

$$\delta H_i^{\circ\ddagger}(\text{TS}) = \delta \Delta H^\ddagger + \delta H_i^{\circ\ddagger}(\text{IS})$$

The preferential solvation of anionic charge in the TS predicts a loose TS with a greater degree of bond cleavage for the reactions of PEB than for EBS, and also for the reactions with BA compared to the reactions with AN.

Introduction

The use of activation parameters, such as ΔH^\ddagger , as experimental tools for the study of solvent effect on the organic reaction mechanism is complicated by the fact that the parameters are themselves differential terms. Arnett and co-workers¹ have measured calorimetrically the "instantaneous" enthalpy of solution of the reacting substrate in the solvent before the chemical reaction has proceeded to any significant extent. Using the enthalpy of solution of the reacting substrate in a series of solvent mixtures, one can define the transfer enthalpy from a reference solvent ($X=0$) to other solvent mixtures (X) for the initial state, $\delta H_i^{\circ\ddagger}$ (IS), and the differential enthalpy of activation, $\delta \Delta H^\ddagger$, determined kinetically can be dissected into its component parts,

$$\delta \Delta H^\ddagger = \delta H_i^{\circ\ddagger}(\text{TS}) - \delta H_i^{\circ\ddagger}(\text{IS}) \quad (1)$$

\uparrow \uparrow \uparrow
 kinetic derived calorimetric

i.e., initial (IS) and transition states (TS), Eq. (1).² In this work, symbols δ and Δ are used to denote the changes in the quantities following due to solvent composition and state of the system, respectively.

Arnett and co-workers¹ reported the first dissection of this type for the ΔH^\ddagger for solvolysis of *t*-butyl chloride in water-ethanol mixtures. The deep minimum found in $\delta \Delta H^\ddagger$ at *ca.* 0.1 mole fraction ethanol has been ascribed to very pronounced maximum in $\delta H_i^{\circ\ddagger}$ (IS) as a function of solvent composition.

Abraham,³ however, dissected solvent effects in terms of the Gibbs free energy and attempted to estimate the position of the TS along the reaction coordinate by comparing the variation of the transfer Gibbs free energy of the transition state, $\delta G_i^{\circ\ddagger}$ (TS), with those of the suitable ion-pairs, $\delta G_i^{\circ\ddagger}$ (M^+Y^-).

For example, comparison of $\delta G_i^{\circ\ddagger}$ (TS) with solvent effects on the equilibria $\text{Et}_3\text{N} + \text{EtI} \rightleftharpoons \text{Et}_4\text{N}^+ \text{I}^-$ and $\text{Et}_3\text{N} + \text{EtI} \rightleftharpoons \text{Et}_4\text{N}^+ + \text{I}^-$, *i.e.*, $\delta G_i^{\circ\ddagger}$ ($\text{Et}_4\text{N}^+ \text{I}^-$) and $\delta G_i^{\circ\ddagger}$ ($\text{Et}_4\text{N}^+ + \text{I}^-$), has

led them to conclude that the $\text{Et}_3\text{N}\text{-EtI}$ TS lies between the reactants and the ion pair, rather closer to the reactants than to the latter, and the pairs of ions is far away from the TS on the reaction coordinate.

In general, however, enthalpy and/or entropy gives much sharper responses to the perturbations introduced into the reaction system than the Gibbs free energy.⁵

In this work, we carried out calorimetric measurements for the reactants to obtain $\delta H_i^{\circ\ddagger}$ (IS) values and also performed kinetic measurements to determine the $\delta \Delta H^\ddagger$ values for the reactions of ethyl (EBS) and 2-phenylethyl benzenesulfonates (PEB) with anilines (AN) and benzylamine (BA) in acetonitrile-methanol mixtures. Using the various derived values, $\delta \Delta G^\ddagger$, $\delta \Delta S^\ddagger$ and $\delta H_i^{\circ\ddagger}$ (TS), we have discussed the solvent effect on the TS structure for the two pairs of reactions, Eq. (2).



Experimental

Materials. Solvents and amines, aniline and benzylamine, were purified by standard methods as described previously.⁶ Ethyl(EBS) and 2-phenylethyl benzenesulfonates (PEB) were prepared as reported.⁷

Density Measurements. EBS and PEB are in liquid state at room temperature. It is therefore necessary to know density for volume-weight conversion. A series of volumes of EBS and PEB in a gas-tight micro-syringe were weighed and the densities were determined from the slopes of linear plots of weight versus volume: $d_{\text{EBS}} = 1.21 \text{ g/mL}$ and $d_{\text{PEB}} = 1.19 \text{ g/mL}$, at 25.0 °C.

Kinetic Procedures. The concentration of amine was kept to 50-100 times of substrate concentration which was $1.0\text{-}1.5 \times 10^{-4} \text{ M}^{-1}$. Following the similar procedures reported earlier,⁷ the second order rate constants, k_2 , were determined

Table 1. Heats of solution of aniline and benzylamine in pure solvents (kcal mol⁻¹)

	AN	BA
in H ₂ O	0.45	-2.31
CH ₃ OH	-0.61	-2.75
CH ₃ CN	0.03	0.44

Table 2. Solute hydrogen-bond basicities $\Sigma\beta_{\text{H}}^{\text{H}}$, and acidities $\Sigma\alpha_{\text{H}}^{\text{H}}$, for amines and solvents

	$\Sigma\beta_{\text{H}}^{\text{H}}$	$\Sigma\alpha_{\text{H}}^{\text{H}}$
AN	0.41	0.26
BA	0.72	0.10
H ₂ O	0.35	0.82
MeOH	0.47	0.43
MeCN	0.32	0.07

at three temperatures, 45.0, 55.0 and 65.0 ± 0.05 °C. Rate constants were determined at least in triplicate and the average values were adapted. The k_2 values were reproducible to within ± 3%.

Calorimetric Measurements. Heats of solution were measured as described previously using LKB-2277 TAM (Sweden, twin isoperibol calorimeter) at 25.0 ± 2 × 10⁻⁴ °C.⁸ Final concentrations of neutral bases and substrates were 5.0 × 10⁻³–2.0 × 10⁻² mol dm⁻³. All calorimetric measurements were carried out more than three times each at four different solute concentrations under no stirring condition. The measured heats of solution were within ± 2% of the average values reported.

Results and Discussion

Transfer Enthalpies of the Initial State, $\delta H_i^{\text{TS}}(\text{IS})$.

Heats of solution of aniline (AN) and benzylamine (BA) in pure solvents are compared in Table 1. The solute hydrogen-bond acceptor basicities, $\Sigma\beta_{\text{H}}^{\text{H}}$, and donor acidities, $\Sigma\alpha_{\text{H}}^{\text{H}}$,⁹ are summarized in Table 2. Both AN and BA are very weak hydrogen-bond donors but BA is a very strong hydrogen-bond acceptor while AN is a moderate acceptor. As a result, BA dissolves in H₂O and CH₃OH exothermically since both H₂O and CH₃OH are good donors. However, AN exhibits little effects in both solvents due to its relatively weak acceptor basicity which is comparable to that of H₂O and CH₃OH.

Since CH₃CN is a weak acceptor with negligible donor ability, both AN and BA, being moderate to strong acceptors, have low heats of solution.

The transfer enthalpies of solute, ethyl (EBS) and 2-phenylethyl benzenesulfonate (PEB), and amines, AN and BA, from acetonitrile (X=0) to acetonitrile-methanol mixtures (X) are summarized in Table 3, together with the transfer enthalpies of initial state, $\delta H_i^{\text{TS}}(\text{IS})$. The transfer enthalpies of amines, AN and BA, are exothermic due to the good H-bond donor property (Table 2) of CH₃OH combined with the good H-bond acceptor properties of AN and BA. The $\delta H_i^{\text{TS}}(\text{BA})$ value is more negative (more exothermic) than that of AN due to the stronger solute H-bond acceptor basicity of BA. We note that δH_i^{TS} exhibits a minimum at X=0.921 and X=0.565 for AN and BA respectively. On the other hand the transfer enthalpies of substrate, EBS and PEB, are all positive and the endothermicity increases with the MeOH content (as X increases). This shows that the substrates are acting as structure breaker for MeOH, i.e., the cavity formation energy increases with MeOH content. The transfer enthalpies of the initial state, i.e., $\delta H_i^{\text{TS}}(\text{IS}) = \delta H_i^{\text{TS}}(\text{amine}) +$

Table 3. Transfer enthalpies (MeCN → Mix) in kcal mol⁻¹ of initial states, $\delta H_i^{\text{TS}}(\text{IS})$, at 25.0 °C

(v/v%) MeOH	(mole fraction of X _{MeOH})	EBS PEB	δH_i^{TS}		$\delta H_i^{\text{TS}}(\text{IS})$	
			AN	BA	AN + EBS AN + PEB	BA + EBS BA + PEB
100	(1.00)	1.64	-0.64	-3.19	1.00	-1.55
		1.54			0.90	-1.65
90	(0.921)	1.25	-0.69	-3.22	0.57	-1.97
		1.13			0.45	-2.09
80	(0.838)	1.06	-0.67	-3.34	0.39	-2.28
		0.86			0.19	-2.48
70	(0.752)	0.80	-0.64	-3.38	0.16	-2.58
		0.56			-0.08	-2.82
50	(0.565)	0.43	-0.55	-3.45	-0.12	-3.02
		0.42			-0.13	-3.03
30	(0.357)	0.26	-0.43	-3.34	-0.17	-3.08
		0.20			-0.23	-3.14
10	(0.126)	0.04	-0.21	-2.29	-0.17	-2.25
		0.05			-0.16	-2.24
0	(0.00)	0.00(1.06) ^a	0.00(0.03) ^a	0.00(0.44) ^a	0.00(1.09) ^a	0.00(1.50) ^a
		0.00(0.83) ^a			0.00(0.86) ^a	0.00(1.27) ^a

^aValues in parenthesis are heats of solution in MeCN.

Table 4. Second order rate constants, k_2 ($\text{dm}^3 \text{mol}^{-1} \text{sec}^{-1}$), variations of activation parameters $\delta \Delta H^\ddagger$ (kcal mol^{-1}), $\delta \Delta S^\ddagger$ ($\text{cal deg}^{-1} \text{mol}^{-1}$) and $\delta \Delta G^\ddagger$ (kcal mol^{-1}), and transfer enthalpies of the TS, $\delta H_i^{\ddagger-\ddagger}(\text{TS})$, for the reactions of ethyl benzenesulfonate (EBS) with aniline (AN) and benzylamine (BA) in acetonitrile-methanol mixtures

Ethyl Benzenesulfonate with Aniline ($k_2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$)									
(v/v%) MeOH	mole fraction of X_{MeOH}	25.0 ° ^b	45.0 °	55.0 °	65.0 °	$\delta \Delta H^\ddagger$	$\delta \Delta S^\ddagger$	$\delta \Delta G^\ddagger$	$\delta H_i^{\ddagger-\ddagger}(\text{TS})$
100	(1.00)	1.45	8.89	22.4	45.0	2.3	12.4	-1.4	3.3
90	(0.921)	1.70	8.65	21.1	37.6	0.7	7.3	-1.5	1.3
80	(0.838)	1.58	7.92	19.2	34.8	0.8	7.5	-1.4	1.2
70	(0.752)	1.41	7.23	17.4	31.5	0.7	7.0	-1.4	0.9
50	(0.565)	1.14	5.80	13.4	24.9	0.6	6.0	-1.3	0.5
30	(0.357)	0.840	4.25	9.67	18.1	0.5	5.1	-1.1	0.3
10	(0.126)	0.496	2.42	5.92	10.2	0.4	5.1	-0.7	0.2
0	(0.00)	0.148	1.66	3.68	6.76	(14.4) ^a 0.0	(-36.8) ^a 0.0	(25.4) ^a 0.0	0.0

Ethyl Benzenesulfonate with Benzylamine ($k_2 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$)									
(v/v%) MeOH	mole fraction of X_{MeOH}	25.0 ° ^b	45.0 °	55.0 °	65.0 °	$\delta \Delta H^\ddagger$	$\delta \Delta S^\ddagger$	$\delta \Delta G^\ddagger$	$\delta H_i^{\ddagger-\ddagger}(\text{TS})$
100	(1.00)	0.289	1.62	4.18	9.91	5.2	14.5	0.9	3.6
90	(0.921)	0.235	1.72	4.54	10.1	4.7	13.3	0.9	2.7
80	(0.838)	0.256	1.84	4.77	10.6	4.5	12.8	0.8	2.2
70	(0.752)	0.311	2.08	5.09	11.2	3.8	10.8	0.7	1.2
50	(0.565)	0.358	2.29	5.59	11.9	3.4	10.2	0.5	0.4
30	(0.357)	0.451	2.70	6.13	13.1	2.7	7.7	0.5	-0.4
10	(0.126)	0.730	3.36	7.41	13.2	0.5	1.2	0.2	-1.8
0	(0.00)	0.893	3.94	8.23	14.8	(13.6) ^a 0.0	(-31.5) ^a 0.0	(22.9) ^a 0.0	0.0

^aValues in parenthesis are the activation parameters in MeCN. ^bExtrapolated from data at higher temperatures.

$\delta H_i^{\ddagger-\ddagger}(\text{substrate})$, are negative over the whole range for the reactions with BA due to stronger H-bond accepting ability of BA, whereas they are negative only for the MeCN-rich region for the reactions with AN because of weak H-bond acceptor ability of AN combined with increasing cavity formation energy for the substrate with the increase in MeOH content. In both cases, however, $\delta H_i^{\ddagger-\ddagger}(\text{IS})$ exhibits a minimum at $X=0.357$, which is a complex sum result of the two quantities, $\delta H_i^{\ddagger-\ddagger}(\text{amine})$ and $\delta H_i^{\ddagger-\ddagger}(\text{substrate})$. As MeOH content increases from pure MeCN, H-bond formation to AN and BA increases, but the H-bond formation is stronger and increases sharply for the stronger base, BA. This is why there is a sharp drop in the MeCN-rich region for the $\delta H_i^{\ddagger-\ddagger}(\text{IS})$ curve for the BA reactions. In the MeOH-rich region the trend of gradual increase in the $\delta H_i^{\ddagger-\ddagger}(\text{IS})$ values due to the increase in the cavity formation energy with MeOH content up to $X_{\text{MeOH}}=1.0$ is similar for both AN and BA reactions, except that the actual values are more negative for the latter.

Transfer Enthalpies of the Transition States, $\delta H_i^{\ddagger-\ddagger}(\text{TS})$. Second order rate constants, k_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$), variations of activation parameters, $\delta \Delta H^\ddagger$ (kcal mol^{-1}), $\delta \Delta S^\ddagger$ ($\text{cal mol}^{-1} \text{deg}^{-1}$) and $\delta \Delta G^\ddagger$ (kcal mol^{-1}) and the derived (from Eq. 1) transfer enthalpies of the TS, $\delta H_i^{\ddagger-\ddagger}(\text{TS})$, are summarized in Tables 4 and 5 for the reactions of EBS and PEB with amines (AN and BA) respectively in MeCN-MeOH

mixtures.

The plots of $\delta H_i^{\ddagger-\ddagger}(\text{IS})$, $\delta H_i^{\ddagger-\ddagger}(\text{TS})$ and $\delta \Delta H^\ddagger$ against solvent composition, X_{MeOH} , are shown in Figures 1-4.

Reference to Tables 4 and 5 reveals that the rate increases (and hence $\delta \Delta G^\ddagger$ decreases) despite the increase in $\delta \Delta H^\ddagger$ with the increase in MeOH content for the reactions with AN, whereas it decreases (and hence $\delta \Delta G^\ddagger$ as well as $\delta \Delta H^\ddagger$ increases) with X_{MeOH} for the reactions with BA. This contrasting trends in the rate with X_{MeOH} for AN and BA can be rationalized as follows: For AN reaction, desolvation energy of AN molecule in the activation process should be small since AN is weakly solvated in the IS due to similar solute H-bond basicities for AN ($\Sigma\beta_H^\ddagger = 0.41$) and MeOH ($\Sigma\beta_H^\ddagger = 0.47$).

However, electrophilic H-bonding assistance for leaving group departure will increase with X_{MeOH} resulting in a rate increase. In contrast, for BA reaction desolvation of strongly H-bonded BA should require considerable energy resulting in retardation of the rate with the increase in X_{MeOH} .

In both reactions of EBS and PEB, the rate of the reaction with AN is entropy controlled whereas it is enthalpy controlled with BA. In line with these behaviors in Tables 4 and 5, there is a good compensatory relation between $\delta \Delta H^\ddagger$ and $\delta \Delta S^\ddagger$ and the isokinetic temperature, β in Eq. 3,¹⁰ is lower for the reaction with AN but

Table 5. Second order rate constants, k_2 ($\text{dm}^3 \text{mol}^{-1} \text{sec}^{-1}$), variations of activation parameters $\delta \Delta H^\ddagger$ (kcal mol^{-1}), $\delta \Delta S^\ddagger$ ($\text{cal-deg}^{-1} \text{mol}^{-1}$) and $\delta \Delta G^\ddagger$ (kcal mol^{-1}), and transfer enthalpies of the TS, $\delta H_i^{\ddagger-\ddagger}(\text{TS})$, for the reactions of 2-phenylethyl benzenesulfonate (PEB) with aniline (AN) and benzylamine (BA) in acetonitrile-methanol mixtures

Phenylethyl Benzenesulfonate with Aniline ($k_2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$)									
(v/v%) MeOH	mole fraction of X_{MeOH}	25.0 °C ^a	45.0 °C	55.0 °C	65.0 °C	$\delta \Delta H^\ddagger$	$\delta \Delta S^\ddagger$	$\delta \Delta G^\ddagger$	$\delta H_i^{\ddagger-\ddagger}(\text{TS})$
100	(1.00)	0.189	1.65	4.17	11.0	4.4	15.7	-0.3	5.3
90	(0.921)	0.191	1.61	4.15	10.5	4.1	14.9	-0.3	4.7
80	(0.838)	0.182	1.51	3.95	9.84	4.0	14.5	-0.2	4.2
70	(0.752)	0.174	1.42	3.69	9.05	3.9	13.9	-0.2	3.8
50	(0.565)	0.168	1.28	3.03	7.57	3.1	11.1	-0.2	3.0
30	(0.357)	0.159	1.09	2.45	5.85	2.1	7.5	-0.1	1.9
10	(0.126)	0.139	0.815	1.67	3.79	0.5	2.0	0.0	0.3
0	(0.00)	0.125	0.675	1.45	2.98	(15.3) ^b 0.0	(34.3) ^b 0.0	(25.5) ^b 0.0	0.0

Phenylethyl Benzenesulfonate with Benzylamine ($k_2 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$)									
(v/v%) MeOH	mole fraction of X_{MeOH}	25.0 °C ^a	45.0 °C	55.0 °C	65.0 °C	$\delta \Delta H^\ddagger$	$\delta \Delta S^\ddagger$	$\delta \Delta G^\ddagger$	$\delta H_i^{\ddagger-\ddagger}(\text{TS})$
100	(1.00)	1.38	4.61	7.98	13.3	4.4	14.3	0.1	2.8
90	(0.921)	1.38	4.90	8.62	14.9	3.9	12.4	0.1	1.8
80	(0.838)	1.39	5.23	9.50	16.8	2.7	8.5	0.1	0.2
70	(0.752)	1.41	5.60	10.6	18.9	1.7	5.4	0.0	-1.1
50	(0.565)	1.63	6.49	12.2	22.0	1.7	5.5	0.0	-1.3
30	(0.357)	1.67	7.39	14.4	27.4	1.2	3.7	0.0	-1.9
10	(0.126)	1.69	8.49	17.4	35.1	0.6	1.8	0.0	-1.6
0	(0.00)	1.79	9.45	20.5	47.5	(10.7) ^b 0.0	(37.7) ^b 0.0	(22.0) ^b 0.0	0.0

^aValues in parenthesis are the activation parameters in MeCN. ^bExtrapolated from data at higher temperatures.

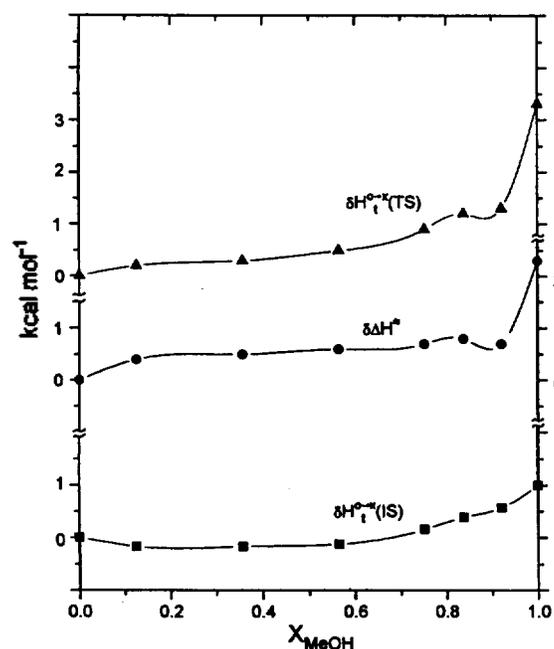


Figure 1. Variation of activation enthalpy ($\delta \Delta H^\ddagger$) and transfer enthalpies of initial state ($\delta H_i^{\ddagger-\ddagger}$) and transition state ($\delta H_i^{\ddagger-\ddagger}$) for the reaction of EBS with AN in MeOH-MeCN mixtures at 25.0 °C.

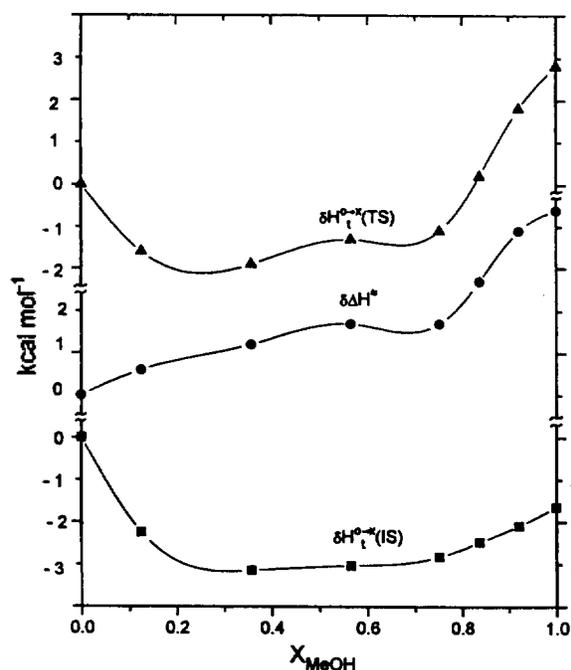


Figure 2. Variation of activation enthalpy ($\delta \Delta H^\ddagger$) and transfer enthalpies of initial state ($\delta H_i^{\ddagger-\ddagger}$) and transition state ($\delta H_i^{\ddagger-\ddagger}$) for the reaction of EBS with BA in MeOH-MeCN mixtures at 25.0 °C.

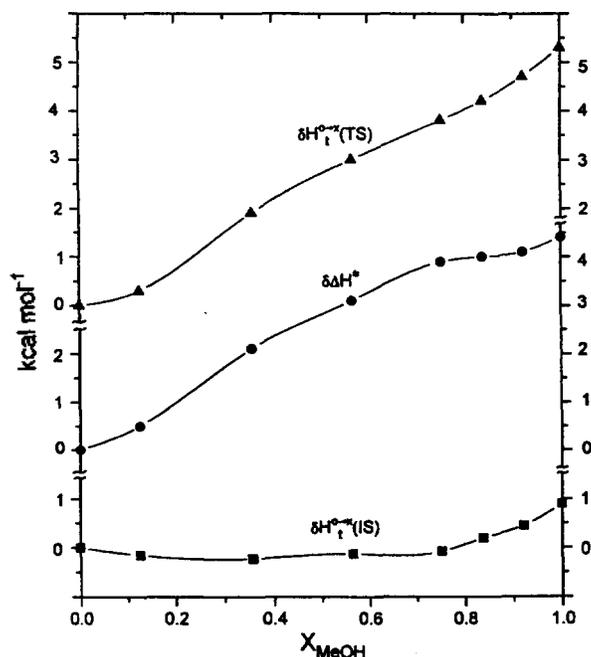


Figure 3. Variation of activation enthalpy ($\delta \Delta H^*$) and transfer enthalpies of initial state ($\delta H_i^{\ddagger}(\text{IS})$) and transition state ($\delta H_i^{\ddagger}(\text{TS})$) for the reaction of PEB with AN in MeOH-MeCN mixtures at 25.0 °C.

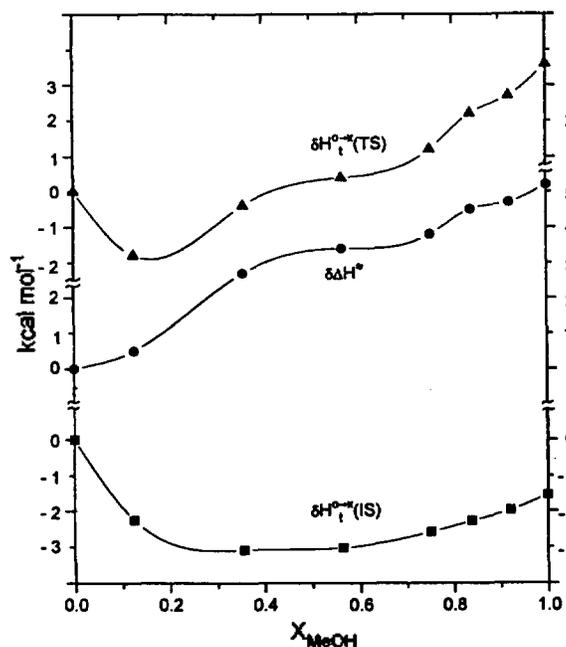


Figure 4. Variation of activation enthalpy ($\delta \Delta H^*$) and transfer enthalpies of initial state ($\delta H_i^{\ddagger}(\text{IS})$) and transition state ($\delta H_i^{\ddagger}(\text{TS})$) for the reaction of PEB with BA in MeOH-MeCN mixtures at 25.0 °C.

$$\delta \Delta H^* = \beta \delta \Delta S^* \quad (3)$$

higher for the BA reaction than the experimental temperature; $\beta = 175$ K and 280 K for AN reaction with EBS and PEB and $\beta = 351$ K and 309 K for BA reaction with EBS

and PEB, respectively.

For the reactions of AN (Figures 1 and 3), the trend of change with solvent in the transfer enthalpy of the TS, $\delta H_i^{\ddagger}(\text{TS})$, follows closely that of $\delta \Delta H^*$ indicating that the solvent effect on the enthalpy of activation, $\delta \Delta H$, is mainly due to that on the TS with little initial state contribution.

Thus in the AN reactions, the S_N2 TS appears to be relatively tight with weak ionic character. As a result, the activated complex as a whole acts as a simple structure breaker of the H-bonded MeCN-MeOH mixtures. The energy required to break the structure is, however, more than compensated for by an increase in the degree of freedom of the solvent molecules, and part of the free MeOH can then electrophilically H-bond to assist leaving group departure; the net effect is an increase in ΔS^* accompanied by a decrease in ΔG^* with the MeOH content of the solvent mixture.

Examination of Figures 2 and 4 indicates that for the reactions of BA the trend of change with solvent in the transfer enthalpy of the TS, $\delta H_i^{\ddagger}(\text{TS})$, is similar to that of the initial state, $\delta H_i^{\ddagger}(\text{IS})$. Since in the activated complex, the nucleophile, BA, is desolvated and exothermic value of $\delta H_i^{\ddagger}(\text{TS})$ must involve H-bond stabilization of partially charged TS, especially of anionic leaving group. Cox *et al.*,¹¹ have shown that MeCN solvates cation while MeOH solvates anion preferentially in the MeCN-MeOH mixtures.

Comparison of the transfer enthalpies of the TS, $\delta H_i^{\ddagger}(\text{TS})$, for the reactions of EBS and PEB with aniline (Tables 4 and 5) shows that the transfer enthalpies are slightly greater positive values for PEB; this is in line with a greater cavity formation energy required for the more bulky substrate PEB compared with EBS. In fact, the trend shown by $\delta H_i^{\ddagger}(\text{TS})$ in Figures 2 and 4 is similar to variation of transfer enthalpies of relatively bulky ion pairs, Ag^+Cl^- and Ag^+Br^- , from MeCN to MeCN-MeOH mixtures. The similarity between the two can be interpreted as follows: The S_N2 TS, which can be considered as a weakly charged ion-pair state, $\text{R}^{\delta+} \cdots \text{X}^{\delta-}$, is stabilized by the preferential solvation of cationic charge, $\text{R}^{\delta+}$, ($\text{R} = \text{CH}_2\text{CH}_2$ or $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$) by acetonitrile and of the leaving group, $\text{X}^{\delta-}$ ($\text{X} = \text{OSO}_2\text{C}_6\text{H}_5$), by methanol exhibiting a similar trend to that shown for the variation of transfer enthalpies of Ag^+Cl^- . The response *i.e.*, the well depth, is however very shallower than that for the fully developed ion-pair due most probably to the lower charge development in the TS. The broad well for the plot of $\delta H_i^{\ddagger}(\text{TS})$ versus X_{MeOH} is somewhat deeper for the reaction of PEB than that of EBS with BA suggesting that the TS for the reaction of PEB is somewhat looser with a greater degree of bond cleavage and hence with a greater degree of charge development. This is in accord with the conclusion reported previously.^{7b}

In summary, the preferential solvation of anionic charge by MeOH and of cationic charge by MeCN in the TS predicts a looser TS with a greater degree of bond cleavage for the reactions of 2-phenylethyl rather than for ethyl benzenesulfonate. The reaction with a stronger base, benzylamine, is characterized by a later TS compared to that with a weaker base, aniline.

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Dehydrogenative Polymerization of New Alkylsilanes Catalyzed by $Cp_2MCl_2/Red-Al$ System ($M=Ti, Hf$): Synthesis of Poly(substituted 3-phenyl-1-silabutanes)

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Substituted 3-phenyl-1-silabutanes such as 3-phenyl-1-silabutane (1), 3-(2,5-dimethylphenyl)-1-silabutane (2), 3-(p-chlorotolyl)-1-silabutane (3), and 3-naphthyl-1-silabutane (4) were prepared in 62-96% yield by reduction of the corresponding substituted 3-phenyl-1,1-dichloro-1-silabutanes with $LiAlH_4$. The dehydrogenative polymerization of the monomer silanes was carried out with $Cp_2MCl_2/Red-Al$ ($M=Ti, Hf$) catalyst system. The molecular weight of the polymers produced ranged from 700 to 1300 (*vs* polystyrene) with degree of polymerization (DP) of 5 through 16 and with polydispersity index (PDI)=1.1-2.1. The dehydrogenative polymerization of the monomer silanes with $Cp_2TiCl_2/Red-Al$ catalyst system occurred at a faster rate and produced somewhat higher molecular weights of polysilane than that with $Cp_2HfCl_2/Red-Al$ catalyst system.

Introduction

Polysilanes have received a considerable amount of attention as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators.¹⁻³ The only viable method to get high molecular weight polysilanes to date has been the Wurtz coupling reaction of dichlorosilanes, which has several commercial drawbacks.

A major breakthrough in polyorganosilane synthesis was Harrod's recent discovery of the group 4 metallocene-catalyzed dehydrogenative polymerization.⁴ Two mechanisms have been so far proposed: (1) the oxidative addition/reductive

elimination sequences *via* the intermediacy of transition-metal silylene complexes⁴ and (2) the four-center sigma bond metathesis processes among silicon, hydrogen, and a d^0 metal center *via* the intermediacy of transition-metal silyl and hydride complexes.⁵ The latter mechanism is strongly supported by many model reactions⁵ and thermochemical results.⁶

A major disadvantage of the metallocene-catalyzed dehydrogenative coupling method is to produce low molecular weights of polysilanes.^{4,5} Copious efforts have been made to increase the molecular weight of the polysilanes: (1) employment of multi(silyl)arene as a cross-linking agent,⁷ (2) polymerization of sterically less hindered silanes such as SiH_4 ,