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Note

The calorimetric determination of enthalpies of transfer of halide ions in aqueous dimethyl sulfoxide solutions

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ABSTRACT

The solvation of chloride, bromide, and iodide ions in dimethyl sulfoxide is only slightly affected by the addition of water up to the composition DMSO·H_2O. The large tetra-*n*-butylammonium ion suffers dessolvation, which reflects increasing solvent–solvent interactions.

INTRODUCTION

The transfer of many reactions involving anions (including bimolecular nucleophilic substitutions) from polar aprotic solvents to protonic solvents results in sharply reduced reaction rates[1]. In the S_N2 reaction:

$$Nu^- + RX \rightarrow [Nu\cdots R\cdots X]^- \rightarrow NuR + X^-,$$

a complete analysis of solvent effects must consider the solvation of Nu^-, RX, and the transition state, $NuRX^-$. In the great majority of substitutions at saturated carbon solvation of the anionic nucleophile is by far the most important of these factors. Even the less drastic transfer from aqueous dimethyl sulfoxide (DMSO) of composition DMSO·$2H_2O$ to pure water decreases the rates of the methyl iodide reactions with azide, cyanide, and thiocyanate to only 0.05 of the original. Increased anion solvation in water is mainly responsible. The addition of water to the reaction of *n*-propyl tosylate (*p*-toluenesulfonate) with halide ions in DMSO similarly reduces the substitution rates. Chloride ion in aqueous DMSO (DMSO·H_2O) reacts at only 0.07 the rate in pure DMSO[2].

We were interested in whether the addition of water to DMSO results in sufficiently stronger solvation of the halide ions to account for the decreased reactivity towards propyl tosylate in aqueous mixtures.

EXPERIMENTAL

The calorimeter and the procedure used in determining enthalpies of solution have previously been described[3]. Enthalpies of solution in DMSO, 95%, 90%, 85%, and 80% DMSO (+water, v/v) were determined at 25°C for tetrabutylammonium tetrabutylborate, chloride, bromide, and iodide, and for *n*-propyl tosylate. The preparation and purification of the salts and solvents were those previously used[4]. Each heat of solution reported is the average of 3–5 determinations in the concentration range 3×10^{-5} to 4×10^{-4} *M*. No dependence of the molar enthalpy of solution on concentration was observed within this range.

RESULTS AND DISCUSSION

The enthalpy of transfer ($\Delta\Delta H_s$) is the difference in heats of solution of a salt in two solvents. For example, the enthalpy of solution (ΔH_s) of Bu_4NI in DMSO (Table I) is 7.2 kcal/mole, and in 80% DMSO, 8.3 kcal/mole. $\Delta\Delta H_s$ for the transfer from DMSO to 80% DMSO is (8.3)−(7.2) = 1.1 kcal/mole. This means that the overall solvation of Bu_4N^+ and I^- ions is 1.1 kcal/mole less in the aqueous solvent, but this might result from any combination of ionic enthalpies of transfer. To assign individual ionic $\Delta\Delta H_s$ values some extrathermodynamic assumption must be made. Various of these have been used, and the rather good agreement between them gives some confidence in the validity of the assumptions[1,4]. The assumption used in this work is that in the transfer of Bu_4NBBu_4 from one solvent to another, each of these large, equal sized, and diffusely charged ions (Bu_4N^+ and Bu_4B^-) undergoes an equal change in solvation enthalpy. $\Delta\Delta H_s$ for Bu_4NBBu_4 obtained experimentally is therefore twice that for Bu_4N^+ ion:

TABLE I

ENTHALPIES OF SOLUTION[a] IN AQUEOUS DMSO AT 25°C

Solvent (% DMSO)[b]	*Bu$_4$NBBu$_4$*[c]	*Bu$_4$NCl*	*Bu$_4$NBr*	*Bu$_4$NI*	*n-PrOTs*[d]
100	9.9±0.1[e,f]	3.0±0.1[f]	5.1±0.1[f]	7.2±0.2[f]	1.2±0.1
95	11.4±0.1	3.3±0.1	5.7±0.1	7.4±0.2	1.4±0.1
90	10.9±0.3	4.1±0.1	6.1±0.1	7.9±0.1	2.4±0.1
85	13.4±0.1	4.3±0.1	6.6±0.1	8.1±0.2	2.6±0.1
80	13.1±0.3	4.4±0.1	7.1±0.1	8.3±0.1	3.1±0.1
0	−12.0[g]	−7.3±0.1[f]	−2.2±0.1[f]	3.8±0.1[f]	−3.0[h]

[a] Values of ΔH_s in kcal/mole are averages of 3 to 5 determinations. [b] Percent DMSO by volume in mixtures with water; mole percent DMSO in mixtures: 100, 82.7, 69.3, 59.1, 50.3, and 0. [c] Bu is *n*-butyl. [d] *n*-Propyl *p*-toluenesulfonate. [e] The mean value of ΔH_s is followed by the average deviation of the individual values from the mean. [f] Values from Ref. 4. [g] Estimated using Arnett's single ion enthalpies of transfer for halide ions (Ref. 5). [h] Based on one determination only.

Bu_4NBBu_4: $\Delta H_s(\text{DMSO}) = 9.9$, $\Delta H_s(80\%\ \text{DMSO}) = 13.1$; $\Delta\Delta H_s = 13.1 - 9.9 = 3.2$, $\Delta\Delta H_s\ (Bu_4N^+) = 3.2/2 = 1.6$.

Bu_4NI: $\Delta\Delta H_s = 1.1 = \Delta\Delta H_s(Bu_4N^+) + \Delta\Delta H_s(I^-)$;
$\Delta\Delta H_s(I^-) = 1.1 - 1.6 = -0.5$ kcal/mole.

Other single ion enthalpies of transfer (Table II) were similarly obtained. However, we have noted for Bu_4NBBu_4 that a plot of ΔH_s *vs.* solvent composition shows the points deviating slightly from a smooth curve, presumably due to small experimental errors. We have therefore chosen to normalize the system by assuming the correct values for ΔH_s (Bu_4NBBu_4) to be those obtained from the smooth curve. In no case are the normalized values (Table II) more than 0.5 kcal/mole different from the experimental values.

The most striking feature of the data in Table II is the slight change in solvation enthalpy of the halide ions when as much as 20% water is present in the solvent. Although $\Delta\Delta H_s$ (DMSO to water) of chloride ion is −4.3 kcal/mole, only −0.4 kcal/mole change has occurred when DMSO is diluted with equimolar amounts of water (80% DMSO by volume). The slight increase in chloride solvation is insufficient to cause the decreased rate and the increased enthalpy of activation (ΔH^* is 16.5 kcal/mole in DMSO, 17.5 kcal/mole in 80% DMSO[2]). The other factors which are involved are $\Delta\Delta H_s$ of propyl tosylate (1.9 kcal/mole) and $\Delta\Delta H_s$ for the transition state[6]:

$$\Delta\Delta H^* = \Delta\Delta H_s^{ts} - \Delta\Delta H_s^{Cl^-} - \Delta\Delta H_s^{PrOTs}$$

TABLE II

SINGLE ION ENTHALPIES OF TRANSFER[a] FROM DMSO AT 25 °C

Ion	*DMSO (%)*				*H_2O*
	95	*90*	*85*	*80*	
Bu_4N^{+b}	0.5	1.0	1.4	1.8	−6.0
Cl^-	−0.2	0.1	−0.3	−0.4	−4.3
Br^-	0.1	0.0	−0.1	0.2	−1.3
I^-	−0.3	−0.3	−0.7	−0.7	2.6
n-PrOTs[c]	0.2	1.2	1.4	1.9	−4.2

[a] Values in kcal/mole; normalized as described in text. [b] The experimental value in mixed solvents are 0.8, 0.5, 1.8, and 1.6, respectively. [c] $\Delta\Delta H_s$ values directly from ΔH_s without normalization.

The value of $\Delta\Delta H_s^{ts}$ is 2.5 kcal/mole. Desolvation of propyl tosylate is the principal rate accelerating effect. This is outweighed by slight desolvation of chloride ion, and considerable desolvation of the transition state, both of which have rate decreasing effects.

It is generally recognized that small anions are most strongly solvated by hydrogen bonding solvents such as water and methanol, whereas large polarizable anions are best solvated by dipolar aprotic solvents such as DMSO[1]. Very large ions and molecules of limited polarizability (such as Bu_4N^+ ion and propyl tosylate) are poor hydrogen bond and electron pair acceptors, and are incapable of substantial dipole-induced dipole interactions with polar solvents. In the absence of strong solvent–solute interactions the most important factor governing ΔH_s values becomes the energy required to break solvent–solvent interactions to make "holes" for the solute particles. This term becomes more endothermic with increasing strength of the solvent–solvent attractions and with increasing solute size. Transfer of the large species Bu_4N^+ and PrOTs from DMSO to the more highly structured DMSO–water mixtures is, in fact, appreciably endothermic (Table II).

CONCLUSION

The solvation of chloride, bromide, and iodide ions in DMSO is only slightly affected by the addition of water up to the composition $DMSO \cdot H_2O$. Tetrabutylammonium ion and propyl tosylate lose solvation. The rate of reaction of chloride ion with propyl tosylate in DMSO is decreased, and ΔH^* is increased, by the addition of water. This results mainly from desolvation of the transition state.

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