Determination of the Heat of Transfer of the Proton from Water to Dimethylsulfoxide and Pyridine

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The proton is strongly hydrated in aqueous solution due to strong hydrogen bonding [1]. The free energy of transfer ΔG_{tr}°, for the proton from water to dimethylsulfoxide has been reported to be -18.8 kJ mol^{-1} [2]. Dimethylsulfoxide in general solvates hard acceptors very well, and it solvates all ions more strongly than water [2–4], including the proton, in spite of dimethylsulfoxide being an aprotic was determined to be -28 kJ mol^{-1} in pyridine [4]. This value is in close agreement with -24 kJ mol^{-1} calculated from standard electrode potentials in pyridine reported by Mukherjee [5]. Pyridine is known to be a fairly strong base in aqueous solution. Pyridine is therefore expected to solvate the proton well. The proton is very poorly solvated in acetonitrile, $\Delta G_{tr}^{\circ} = +46.2$ and $\Delta H_{tr}^{\circ} = +56.0$ kJ mol^{-1} [2, 6]. Acetonitrile solvates both hard and soft acceptors, except the univalent d^{10} metal ions, poorly [3, 7] due to weak donor properties.

The heats of transfer of the proton from water were determined from the heats of solution of picric acid in water, dimethylsulfoxide and pyridine. Heats of transfer for the picric ion have been determined previously using the tetraphenylarsonium tetraphenylborate (TATB) assumption, stating that $\Delta H_{tr}^{\circ}(\text{AsPh}_4^+) = \Delta H_{tr}^{\circ}(\text{BPh}_4^-)$ [4]. The calculation routines for obtaining heats of transfer of single ions are described elsewhere [4].

Experimental

Chemicals

The purification of water, dimethylsulfoxide (Merck) and pyridine (DeHaën p.a.) has been described elsewhere [3]. Picric acid (Merck p.a.) was recrystallized from acetone and diethylether and dried over phosphorouspentoxide under reduced pressure.

Calorimetric Measurements

The ampoule calorimeter used has been described earlier [8, 9]. The salts were kept in the calorimeter in glass ampoules. In water and dimethylsulfoxide the ampoules were sealed with wax, in pyridine they were sealed by melting the filling tube [4]. The measurements were performed in 80 ml of solvent without supporting electrolyte. At least five experiments, which were in close agreement, were performed. Varying amounts of salt were used in order to check if the heats obtained varied with the concentration. The concentration of salt never exceeded 20 mM. Complete dissociation of picric acid in dilute aqueous and dimethylsulfoxide solution was assumed, pK_a (C$_6$H$_2$(NO$_2$)$_3$OH) = 0.3 in water [10], and = -0.3 in DMSO [11]. Conductivity studies were also performed in a series of five, tenfold consecutive diluted solutions. The logarithmed conductivity was proportional to the logarithmed concentration, and the slope was larger than 0.7 which assured complete dissociation. All experiments were performed at 25.000 ± 0.002 °C.

Results

The heat of solution of picric acid is negative in DMSO and pyridine, while a positive value is obtained in water. The heats of transfer of the proton in the different solvents were determined from the heats of transfer of picric acid and the picric ion. The heats of solution and the heats of transfer of picric acid, the heats of transfer of the picric ion and the transfer thermodynamics of the proton are given in Table I.

Discussion

The heats of solvation can be divided into two main terms; the energy gained at the coordination of solvent molecules to ions or complexes, and the energy consumed when the solvent molecules are forced out of the bulk structure and are made available for coordination [4]. Pyridine is an aprotic solvent and a strong base with low bulk order; the intramolecular forces are weak. The proton is strongly solvated in pyridine with a ΔH_{tr}° value of -43.6 kJ mol^{-1}. The entropy of transfer is negative indicating an increase in order when the proton is leaving an aqueous solution for a pyridine one. This shows that there is a strong bond between pyridine and a proton; the pyridinium ion is known to be stable, and it is a weak acid in aqueous solution.

Domain *et al.* [6] have reported a $\Delta H_{tr}^{\circ}(\text{H}^+)$ value to DMSO of -25.6 kJ mol^{-1}. This value is markedly more negative than the value found in this study, -11.5 kJ mol^{-1}. Several determinations of

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TABLE I. The Heats of Solution, ΔH°_s (kJ mol^{-1}), of Picric Acid in Water, Dimethylsulfoxide (DMSO) and Pyridine; the Heats of Transfer ΔH°_{tr} (kJ mol^{-1}), from Water to DMSO, Pyridine and Acetonitrile (AN) of Picric Acid, the Picric Ion and the Proton; and the Free Energies and Entropies of Transfer, ΔG°_{tr}, $T\Delta S^{\circ}_{tr}$ (kJ mol^{-1}), of the Proton

	ΔH°_s		ΔH°_{tr}		ΔH°_{tr} H$^+$	$T\Delta S^{\circ}_{tr}$ H$^+$
	HPic	HPic	Pic$^-$	H$^+$		
Water	+17.7 ± 0.6					
DMSO	−6.5 ± 0.5	−24.2	−12.7[a]	−11.5	−18.8[b]	+7.3
				−25.6[c]		−6.8
Pyridine	−38.2 ± 2.5	−55.9	−12.3[a]	−43.6	−28[b]	−16
AN				+56.0[c]	+46.2[c]	+9.8

[a]Ref. 3.   [b]Ref. 4.   [c]Ref. 6.

ΔG°_{tr}(H$^+$) to DMSO have given values close to the selected one, -18.8 kJ mol^{-1} [3]. The entropy of transfer of the proton from water to DMSO will be negative if the ΔH°_{tr} value from this study is used, while it becomes positive if the value reported by Domain *et al.* is used, Table I.

Solvents, which are weak bases like acetonitrile, DMSO and water, solvate the proton through hydrogen bonds if such can be established in the solvent. Water is known to form strong hydrogen bonds and it solvates the proton mainly through these. DMSO has also a possibility to form hydrogen bonds through its oxygen atom. The hydrogen bonds to DMSO are of course much weaker than in water. Acetonitrile has no possibilities to form hydrogen bonds and it is at the same time a very weak base. The proton is therefore very weakly solvated in acetonitrile, Table I.

Hydrogen bonds will bring order to a system. The change in degree of order in a solvent by introducing protons will therefore be proportional to the strength of the hydrogen bonds. From this point of view the entropy of transfer will increase in the order acetonitrile < DMSO < pyridine. At the same time, all studied univalent ions are more strongly solvated in DMSO than in water [3, 4]. It is therefore difficult from the entropies of transfer to judge if

our value of ΔH°_{tr} or that of Domain *et al.* is the correct one.

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