

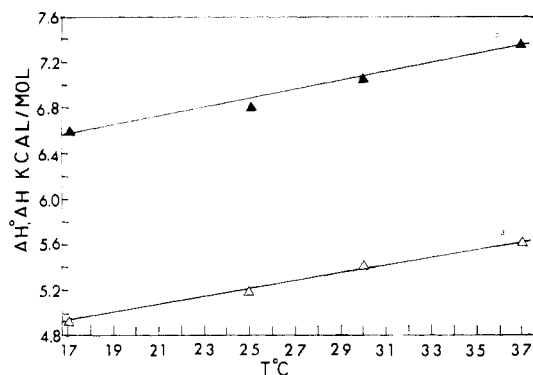
Table I. Enthalpies of Solution

t , °C	runs	ΔH° and ΔH , cal/mol	t , °C	runs	ΔH° and ΔH , cal/mol
Uridine-H ₂ O			Cytidine-H ₂ O		
17	7	4980 ± 39	18	7	4991 ± 46
25	5	5197 ± 24	25	6	5296 ± 26
30	10	5414 ± 23	30	6	5320 ± 50
37	13	5625 ± 42	37	6	5525 ± 36
Uridine-3 <i>m</i> Ethanol			Cytidine-3 <i>m</i> Ethanol		
17	7	6600 ± 19	18	5	6538 ± 22
25	7	6795 ± 13	25	9	6733 ± 27
30	12	7037 ± 47	30	8	6828 ± 34
37	13	7384 ± 70	37	6	6908 ± 34

Table II. Enthalpies of Transfer at 25 °C and Heat Capacities of Solution and Transfer at 17–35 °C

solute	$\Delta \bar{H}^a$, kcal/mol	ΔC_p° ^b	ΔC_p^b	$\Delta \bar{C}_p^\circ$ ^c cal/(mol deg)
uridine	1.60	35	37	2
cytidine	1.46	28	22	-6

^aOverall experimental error is ± 0.05 kcal/mol, based on the rounded-off value of the square root of the sums of the squares of the standard deviations of the means of ΔH° and ΔH . ^bOverall experimental error is ± 8 cal/(mol deg), based on the average difference between worst and chosen slopes of Figures 1 and 2. ^cValues are almost negligible, based on overall experimental errors.^b

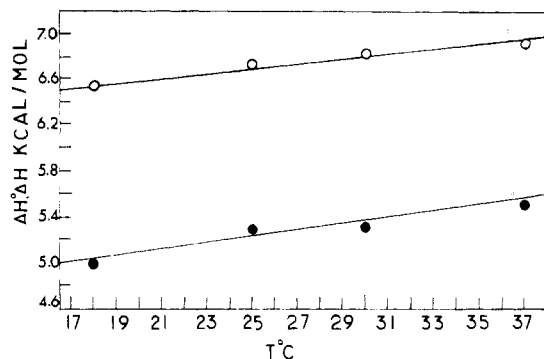
Figure 1. Enthalpies of solution of uridine: (a) in H₂O; (b) in 3 *m* ethanol.

Sigma. Ethanol was AR grade and the water was distilled and deionized. The overall range was 0.4–0.9 mmol of nucleoside dissolved in 180 g of solvent. The average of four or more measurements is reported as the enthalpy of solution at infinite dilution, with uncertainties equal to the standard deviation of the means.

Results and Discussion

Table I and Figures 1 and 2 show the means of the enthalpies of solution for both nucleosides in pure water and in 3 *m* ethanol. Table II reports enthalpies of transfer at 25 °C, $\Delta \bar{H}$, together with heat capacities of solution ΔC_p° , ΔC_p , and transfer, $\Delta \bar{C}_p^\circ$, based on the slopes of the linear enthalpies of solution from Figures 1 and 2.

It is of interest to compare the separate enthalpies of transfer of the appropriate free base and ribose with the total $\Delta \bar{H}$ of the nucleoside. Preliminary measurements show that the enthalpies of transfer of cytosine and ribose (5) are 0.7 and 1.0 kcal/mol, respectively, with their sum 0.2 kcal/mol higher than that of cytidine. The positive difference may be due to changes in size, conformation, and solvation of the two constituents relative to the single nucleoside. The large positive values of $\Delta \bar{H}$ may reflect in part the energy difference of solute cavity formation in pure water and in the more structured aqueous ethanol (6).

Figure 2. Enthalpies of solution of cytidine: (a) in H₂O, (b) in 3 *m* ethanol.

The heat capacities of transfer $\Delta \bar{C}_p^\circ$ of each nucleoside are almost negligible, within the limits of the overall experimental error. If the ordering of the solvents around the nucleosides contributes to their partial molal heat capacities \bar{C}_p° in water or \bar{C}_p in 3 *m* ethanol ($\Delta \bar{C}_p^\circ = \bar{C}_p^\circ - \bar{C}_p^\circ$), this result indicates that the difference is very small, whatever the detailed nature of ordering in the two solvent media may be. Heat capacities of the solid nucleosides, $C(s)$, are needed in order to calculate the partial molal heat capacities, where $\bar{C}_p^\circ = \Delta C_p + C(s)$, and $\bar{C}_p = \Delta C_p + C(s)$. In the absence of reported values, $C(s)$ was estimated by Benson's method of group addivities (7). Since these group contributions at 25 °C are for the ideal gas, the following estimates include corrections for loss of translational and rotational degrees of freedom of the gas offset by the gain of vibrational degrees of freedom of the solids. When a group value was not available, a tabulated one for a similar group was substituted. The method was tested on solid uracil, one of the very few related substances for which the experimental $C(s)$ is available (8), with estimated and experimental values of 29 and 28 cal/(mol deg), respectively. Kopp's law, which was used previously with inosine and adenosine (1), gives 34 cal/(mol deg). The estimated values of $C(s)$ are 61 and 65 cal/(mol deg) for uridine and cytidine, yielding 96 and 93 cal/(mol deg) for their partial molal heat capacities in pure water, respectively. This difference between values of \bar{C}_p° is negligible, and thus partial molal heat capacities in pure water seem to be almost independent of the bonding and functional group differences of the two nucleosides. In 3 *m* ethanol the partial molal heat capacities for uridine and cytidine are 98 and 87 cal/(mol deg). The somewhat larger difference shows that ethanol appears to reduce the leveling effect on the heat capacities in pure water, with similar behavior observed earlier with inosine and adenosine (1).

Acknowledgment

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Registry No. Uridine, 58-96-8; cytidine, 65-46-3; ethanol, 64-17-5.

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