# Single Ion Enthalpies of Transfer from Methanol to Dimethyl Sulfoxide, N,N-Dimethylformamide, N-Ethylacetamide, and N-Methylpyrrolidinone

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**Abstract:** Enthalpies of solution ($\Delta H_s$) of 16 organic and inorganic salts have been measured in methanol, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), N-methylpyrrolidinone (NMP), N-ethylacetamide (NEA), and water, and of the lithium halides in hexamethylphosphoric triamide (HMPT). Single ion enthalpies of transfer ($\Delta\Delta H_s$) from methanol to the other solvents have been calculated on the basis of three different extrathermodynamic assumptions: $\Delta\Delta H_s((C_4H_9)_4N^+) = \Delta\Delta H_s(^-B(C_4H_9)_4)$, $\Delta\Delta H_s((C_5H_{11})_4N^+) = \Delta\Delta H_s(^-B(C_5H_{11})_4)$, and $\Delta\Delta H_s((C_6H_5)_4As^+) = \Delta\Delta H_s(^-B(C_6H_5)_4)$. There is good agreement in all cases between single ion enthalpies of transfer calculated from the first two assumptions, but values based on the tetraphenylarsonium tetraphenylborate assumption show deviations. Some $\Delta H_s$ values in the solvents water, methanol, DMF, and NEA are concentration dependent and have been extrapolated to zero concentration. The present values of $\Delta H_s$ (at $c = 0$) for $(C_4H_9)_4NB(C_4H_9)_4$ in methanol and DMF are quite different from some recently reported values[12] measured at higher concentrations.

The observations that many nucleophilic displacement reactions proceed at faster rates in dipolar aprotic solvents than in protic ones[2-5] and that the nucleophilicity of the halide ions in water ($I^- > Br^- > Cl^-$) is reversed[2,3] in dipolar aprotic solvents have led to the suggestion that small anions are poorly solvated in dipolar aprotic solvents,[6-8] but that large polarizable anions (and hence SN2 and SNAr transition states) are more solvated by dipolar aprotic solvents than by protic ones.[2,7,8] In order to determine the extent of ion solvation in different solvents, investigators[9-13] have made use of various extrathermodynamic assumptions to calculate single ion enthalpies of transfer and single ion solvent activity coefficients. The two most commonly used assumptions are: (a) if two ions of opposite charge are of similar structure, and the charges are well shielded by substituents such that there is low charge density on the surface of the ions, then the enthalpy of transfer and solvent activity coefficient difference between two solvents are the same for each ion. Examples of these ions are: (1) $(C_6H_5)_4P^+ = {}^-B(C_6H_5)_4$;[9] (2) $(C_6H_5)_4As^+ = {}^-B(C_6H_5)_4$;[11] (3) $(n\text{-}C_4H_9)_4N^+ = {}^-B(n\text{-}C_4H_9)_4$.[12] (b) The enthalpy of transfer and solvent activity coefficient difference of an ion is the same as that for a neutral molecule, if the ion is well shielded by substituents and has low surface charge density. Examples of these are: (1) $(C_6H_5)_4B^- = (C_6H_5)_4C$;[9] (2) $I_2 = I_3^-$.[13]

Arnett and McKelvey[11] have used the tetraphenylarsonium tetraphenylborate assumption to demonstrate, through single ion enthalpies of transfer, that water is a better solvating medium for small anions than for large ones and that the degree of solvation of the halide ions in water is in the order $Cl^- > Br^- > I^-$. The single ion enthalpies of transfer from water to DMSO are $I^-$ (exothermic) $< 0 < Br^- < Cl^-$. This indicates that the smaller anions ($Cl^-$ and $Br^-$) lose in solvation and $I^-$ gains in solvation in the transfer. Friedman[14] has calculated single ion enthalpies of transfer from water to propylene carbonate with results similar to those of Arnett,[11] *i.e.*, large anions such as $I^-$ and $ClO_4^-$ gain in solvation while small anions such as $Cl^-$ lose in solvation in the transfer.

Parker[13] has used all of the assumptions listed above plus a number of others to determine single ion solvent activity coefficients in a number of protic and dipolar aprotic solvents. His work also indicates that small ions lose in solvation and large, polarizable ions gain in solvation in the transfer from protic to dipolar aprotic solvents.

In spite of the fact that large anions gain in solvation in the transfer from protic to dipolar aprotic solvent, the solvation of the halide ions in DMSO[15] (and other solvents used in the present work) is still $Cl^- > Br^- > I^-$.

Recent work[12] on the enthalpies of transfer from methanol to DMF for the transition states of some SN2 and SNAr reactions suggests that an increase in solvation of the transition state may, in some cases, be the most important factor in promoting a faster reaction in

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[1] Author to whom inquiries should be directed. Support of this work by the Robert A. Welch Foundation (Grant E-136) is gratefully acknowledged.

[2] (a) A. J. Parker, *J. Chem. Soc.*, 1328 (1961); (b) J. Miller and A. J. Parker, *J. Amer. Chem. Soc.*, **83**, 117 (1961); (c) W. M. Weaver and J. D. Hutchison, *ibid.*, **86**, 261 (1964); (d) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, **No. 9**, 24 (1960).

[3] K. Mahendran, Ph.D. Dissertation, University of Houston, 1968. (The rates of reaction of eleven nucleophiles with $n$-propyl tosylate in DMSO are reported.)

[4] D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *J. Amer. Chem. Soc.*, **83**, 5835 (1961).

[5] D. Martin, A. Weise, H. J. Niclas, *Angew. Chem. Intern. Ed. Engl.*, **6**, 318 (1967).

[6] J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, **57**, 1796 (1961).

[7] A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

[8] R. Alexander, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **89**, 3703 (1967).

[9] E. Grunwald, G. Baughman and G. Kohnstam, *ibid.*, **82**, 5801 (1960).

[10] O. Popovych, *Anal. Chem.*, **38**, 558 (1966).

[11] E. M. Arnett and D. R. McKelvey, *J. Amer. Chem. Soc.*, **88**, 2598 (1966).

[12] P. Haberfield, L. Clayman, and J. S. Cooper, *ibid.*, **91**, 787 (1969).

[13] For an extensive review and references see: A. J. Parker and R. Alexander, *ibid.*, **90**, 3313 (1968).

[14] Y. C. Wu and H. L. Friedman, *J. Phys. Chem.*, **70**, 501 (1966).

[15] R. F. Rodewald, K. Mahendran, J. L. Bear, and R. Fuchs, *J. Amer. Chem. Soc.*, **90**, 6698 (1968).

**Table I.** Enthalpies of Solution at 25° [a]

| Salt | $H_2O$ | $CH_3OH$ | NEA | DMSO | DMF | NMP | HMPT |
|---|---|---|---|---|---|---|---|
| LiCl | $-8.9^b$ | $-11.4 \pm 0.2$ | $-10.0 + 0.2$ | $-10.9 \pm 0.3^f$ | $-11.8 \pm 0.1$ | $-8.2 \pm 0.1$ | $-12.3 \pm 0.2$ |
| LiBr | $-11.7^b$ | $-13.4 \pm 0.2$ | $-12.0 \pm 0.3$ | $-17.1 \pm 0.1^f$ | $-18.4 \pm 0.2$ | $-14.5 \pm 0.2$ | $-19.7 \pm 0.2$ |
| LiI | $-15.1^b$ | $-16.9 \pm 0.2$ | $-15.8 \pm 0.3$ | $-24.2 \pm 0.3^f$ | $-25.5 \pm 0.3^b$ | $-20.1 \pm 0.3$ | $-24.2 \pm 0.2$ |
| KBr | $4.8^b$ | $0.7^d$ | | $-2.7 \pm 0.1^f$ | $-3.6 \pm 0.1$ | | |
| KI | $4.9^b$ | $0.2^d$ | | $-6.5 \pm 0.1^f$ | $-8.1 \pm 0.1$ | $-6.1 \pm 0.1$ | |
| NaI | $-1.9^b$ | $-7.0^d$ | $-6.5 \pm 0.1$ | $-11.5 \pm 0.1$ | $-12.8 \pm 0.2$ | $-11.0 \pm 0.2$ | |
| $Bu_4NCl^e$ | $-7.3 \pm 0.1$ | | | $3.7 \pm 0.1$ | | | |
| $Bu_4NBr^e$ | $-2.2 \pm 0.1$ | $5.0 \pm 0.2$ | $3.8 \pm 0.1$ | $5.1 \pm 0.1$ | $0.0^c$ | $3.9 \pm 0.1$ | |
| $Bu_4NI^e$ | $3.8 \pm 0.1$ | $10.4 \pm 0.2$ | $9.1 \pm 0.3$ | $7.2 \pm 0.2$ | $2.1^c$ | $6.8 \pm 0.2$ | |
| $Bu_4NBBu_4^e$ | | $14.1^c$ | $8.5 \pm 0.1$ | $9.9 \pm 0.1$ | $2.1^c$ | $4.8 \pm 0.1$ | |
| $Pn_4NBr^e$ | | $7.8 \pm 0.1$ | $6.4 \pm 0.1$ | $9.6 \pm 0.1$ | $2.7^c$ | $6.8 \pm 0.3$ | |
| $Pn_4NI^e$ | | $14.1 \pm 0.3$ | $12.1 \pm 0.2$ | $12.1 \pm 0.3$ | $6.6^c$ | $10.4 \pm 0.2$ | |
| $Pn_4NBPn_4^e$ | | $19.5^c$ | $13.6 \pm 0.3$ | $18.4 \pm 0.3$ | $8.0^c$ | $10.1 \pm 0.2$ | |
| $Ph_4AsCl$ | $-4.1^c$ | $5.7^c$ | $2.1^c$ | $-1.4 \pm 0.2$ | $-3.5 \pm 0.1$ | $-1.0 \pm 0.1$ | |
| $NaBPh_4$ | $-4.8 \pm 0.1$ | $-3.9^c$ | $-2.5^c$ | $-14.2 \pm 0.2$ | $-19.8 \pm 0.4$ | $-19.0 \pm 0.4$ | |
| $NaClO_4$ | $3.2 \pm 0.1$ | $-2.6 \pm 0.1$ | $-1.6 \pm 0.1$ | $-7.9 \pm 0.1$ | $-10.0 \pm 0.2$ | $-8.8 \pm 0.1$ | |

[a] Values of $\Delta H_s$ in kcal/mol are the average of from 4 to 40 separate runs. [b] Values from National Standards Reference Data System NRSDS-NBS 2. [c] Values from extrapolation of curves obtained by plotting $\Delta H_s$ *vs.* molarity (see text). [d] Values from C. M. Slansky, *J. Amer. Chem. Soc.*, **62,** 2430 (1940). [e] Bu, *n*-butyl; Pn, *n*-pentyl; Ph, phenyl. [f] Values from ref 15. [g] This value is 6.5 kcal/mol more exothermic than a previously published value [L. Weeda and G. Somsen, *Rec. Trav. Chim.*, **76,** 893 (1967)]. Lithium iodide must be very carefully dried.[15]

a dipolar aprotic solvent than in a protic one. A study of the solvation of transition states through solvent activity coefficients[16] shows that solvents such as DMF, DMSO, and HMPT solvate SNAr transition-state anions more strongly than does methanol, but that smaller less polarizable SN2 transition-state anions are more solvated by the protic solvent.

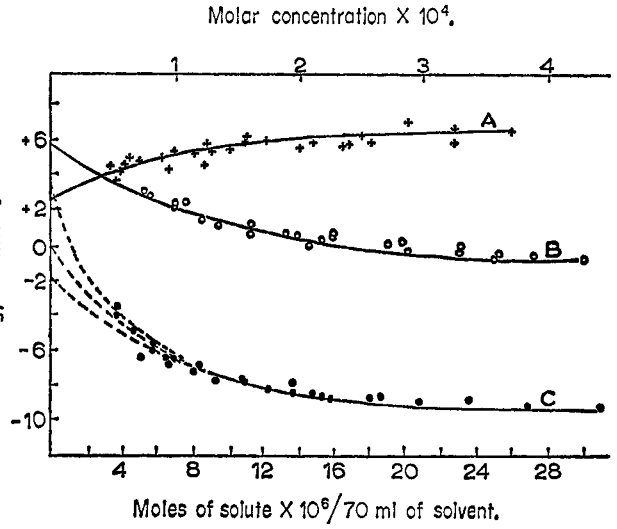

Figure 1. Some concentration-dependent heats of solution: (A) tetrabutylammonium iodide in DMF; (B) tetraphenylarsonium chloride in methanol; (C) sodium tetraphenylborate in methanol.

In an attempt to evaluate some of the extrathermodynamic assumptions, we have determined the enthalpies of solution of 16 organic and inorganic salts in water, methanol, N-ethylacetamide (NEA), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and N-methylpyrrolidinone (NMP), and the values for three lithium halides in hexmethylphosphoric triamide (HMPT). From the heats of solution, single ion enthalpies of transfer from methanol to the other solvents have been calculated, using the extrathermodynamic assumptions $\Delta\Delta H_s((C_4H_9)_4N^+) = \Delta\Delta H_s(^-B(C_4H_9)_4)$, $\Delta\Delta H_s((C_5H_{11})_4N^+) = \Delta\Delta H_s(^-B(C_5H_{11})_4)$, and $\Delta\Delta H_s((C_6H_5)_4As^+) = \Delta\Delta H_s(^-B(C_6H_5)_4)$.[17] The values of enthalpy of solution ($\Delta H_s$) are presented in Table I, and the single ion enthalpies of transfer in Table II. It is important to note that for some of the salts in the solvents water, methanol, DMF, and NEA, the heat of solution (per mole) varies (in some cases strongly) with the concentration of the solute. In these cases we have determined the enthalpies of solution over a wide range of solute concentrations and have plotted $\Delta H_s$ (per mole) *vs.* concentration. The curves obtained were extrapolated to zero concentration. Examples of these curves are shown in Figure 1. While the exact error involved in the extrapolation procedure is unknown, we have grouped the curves according to the probable error. In the first group are those curves which can be extrapolated with an accuracy of 1 kcal or better. This group includes tetraphenylarsonium chloride in water and NEA. These plots are close to linear, but $\Delta H_s$ is still a function of concentration. In the second group are: tetrabutylammonium tetrabutylborate in methanol and DMF, tetrapentylammonium tetrapentylborate in methanol and DMF, tetraphenylarsonium chloride in methanol, tetrabutylammonium and tetrapentylammonium bromides and iodides in DMF. These curves increase in slope more rapidly than those in the first group but are still extrapolated to values which we feel are accurate within 1-2 kcal mole$^{-1}$. The third group of curves contains sodium tetraphenylborate in methanol and NEA. These curve increasingly at low concentrations and could be extrapolated to a wide range of values. We claim an accuracy for the arbitrary extrapolations of no better than ±3-5 kcal mole$^{-1}$. It is surprising that the tetraalkylammonium halides exhibit a concentration dependence in DMF whereas (within experimental error) tetraphenylarsonium chloride does not. Other values of $\Delta H_s$ given in Table I are not concentration dependent.

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(16) (a) A. J. Parker, *Chem. Rev.* **69,** 1 (1969); (b) R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *J. Amer. Chem. Soc.*, **90,** 5049 (1968).

(17) For enthalpies of transfer from water, only the tetraphenylarsonium tetraphenylborate assumption may be used to obtain experimental values since tetrabutylammonium tetrabutylborate and tetrapentylammonium tetrapentylborate are insoluble in water, and the alkali metal tetraalkylborates are not stable in water.

Table II. Single Ion Enthalpies of Transfer[a]

| Ion | $Bu_4N$-$BBu_4$ | $Pn_4N$-$BPn_4$ | $Ph_4As$-$BPh_4$ | $Bu_4N$-$BBu_4$ | $Pn_4N$-$BPn_4$ | $Ph_4$-$AsBPn_4$ |
|---|---|---|---|---|---|---|
| | MeOH → DMSO | | | MeOH → DMF | | |
| $Li^+$ | −6.1 | −6.0 | −2.8 | −6.2 | −6.3 | −2.2 |
| $Na^+$ | −3.4 | −3.1 | +0.1 | −3.5 | −4.1 | −2.1 |
| $K^+$ | −5.6 | −5.6 | −2.2 | −5.5 | −5.8 | −4.5 |
| $Bu_4N^+$ | −2.1 | | | −6.0 | | |
| $Pn_4N^+$ | | −0.55 | | | −5.8 | |
| $Ph_4As^+$ | | | −10.4 | | | −13.8 |
| $Bu_4B^-$ | −2.1 | | | −6.0 | | |
| $Pn_4B^-$ | | −0.55 | | | −5.8 | |
| $Ph_4B^-$ | | | −10.4 | | | −13.8 |
| $Cl^-$ | +6.6 | +6.5 | +3.3 | +5.8 | +5.9 | +4.6 |
| $Br^-$ | +2.2 | +2.4 | −0.9 | +1.0 | +0.3 | 0.0 |
| $I^-$ | −1.1 | −1.45 | −4.5 | −2.3 | −0.7 | −3.6 |
| $ClO_4^-$ | −1.9 | −2.2 | −5.4 | −3.9 | −3.3 | −5.3 |
| | MeOH → NMP | | | MeOH → NEA | | |
| $Li^+$ | −4.5 | −4.5 | −2.2 | −0.4 | +0.1 | +3.5 |
| $Na^+$ | −5.1 | −5.0 | −3.0 | −1.0 | −0.5 | +2.9 |
| $K^+$ | −7.2 | −7.3 | −5.3 | −5.1 | −4.6 | −1.2 |
| $Bu_4N^+$ | −4.7 | | | −2.8 | | |
| $Pn_4N^+$ | | −4.7 | | | −3.0 | |
| $Ph_4As^+$ | | | −12.1 | | | −1.5 |
| $BBu_4^-$ | −4.7 | | | −2.8 | | |
| $BPn_4^-$ | | −4.7 | | | −3.0 | |
| $BPh_4^-$ | | | −12.1 | | | −1.5 |
| $Cl^-$ | +7.7 | +7.7 | +5.4 | +1.7 | +1.4 | −2.1 |
| $Br^-$ | +3.6 | +3.7 | +1.1 | +1.6 | +1.6 | −2.1 |
| $I^-$ | +1.1 | +1.0 | −1.0 | +1.5 | +1.0 | −2.4 |
| $ClO_4^-$ | −1.1 | −1.2 | −3.2 | +2.0 | +1.5 | −1.9 |

[a] Values given in kilocalories per mole.

## Discussion

Of primary importance is the fact that small quantities of water (up to 14 ppm in HMPT) are not responsible for the concentration effects noted above. In DMSO, for example, the water content was about 10 ppm ($5 \times 10^{-5}$ *M*) and no concentration dependence of $\Delta H_s$ was found even though $\Delta H_s$ was measured at salt concentrations as low as $4 \times 10^{-5}$ *M*. Since salt concentrations both less than and greater than water concentration were used and the same $\Delta H_s$ values were observed, any ion solvation by water is not significant. In other solvents, such as methanol and DMF, where water content was 12 and 6 ppm, respectively, some salts such as LiCl (for which preferential ion solvation by water might be expected) showed no concentration effects. Furthermore, $\Delta H_s$ (per mole) for tetraphenylarsonium chloride and sodium tetraphenylborate in methanol become more endothermic at low concentrations (Figure 1). $\Delta H_s$ for these salts is more exothermic in water than in methanol (Table I). The curvature of the methanol plots is in the *opposite* direction of that which would be expected if hydration of the ions were significant at low salt concentrations. Tetrabutylammonium iodide in DMF becomes less endothermic at low concentrations, but the value of $\Delta H_s$ in water suggests that hydration should be more endothermic. (These considerations assume that $\Delta H$ for the ion hydration process will not be greatly different whether it occurs in water, methanol, or DMF). While we are not convinced that the concentration dependence of $\Delta H_s$ results from the presence of ion pairs, we can offer no more convincing explanation at this time.

There is good agreement in all cases between single ion enthalpies of transfer calculated from the tetrabutylammonium tetrabutylborate and the tetrapentylammonium tetrapentylborate assumptions (Table II). Comparison of these two assumptions with the tetraphenylarsonium tetraphenylborate assumption shows fairly consistent deviations which range from about 2 kcal for transfer from methanol to DMF and NMP, to about 3 kcal for transfer from methanol to NEA and DMSO. These deviations can be attributed mainly to the difficult extrapolation of the curve obtained for the plot of concentration *vs.* heat of solution for sodium tetraphenylborate in methanol. A more consistent agreement among the three assumptions is seen in the single ion enthalpies of transfer from NEA to the dipolar aprotic solvents. These values are obtained by dividing $\Delta\Delta H_s$ (NEA to the second solvent) for tetrabutylammonium tetrabutylborate, for example, by 2. This is $\Delta\Delta H_s$ for the tetrabutylammonium ion, which may be substracted from $\Delta\Delta H_s$ of tetrabutylammonium halide to give the single ion enthalpy of transfer for the halide ion, etc. Alternatively, the single ion enthalpies of transfer from NEA to dipolar aprotic solvent may be obtained by subtracting the single ion enthalpies of transfer for methanol to NEA from the values for methanol to dipolar aprotic solvent. Thus, from NEA to DMSO the three assumptions give values falling within a range of only 0.4–0.6 kcal, from NEA to NMP the tetraphenylarsonium tetraphenylborate assumption differs from the other two by about 1–2 kcal, and from NEA to DMF by about 2.5 kcal. To avoid some of the problems which arise due to concentration dependence, one could use the tetraphenyl assumption for enthalpies of transfer from, say, NMP or DMSO to DMF (neither of the tetraphenyl salts is concentration dependent in these solvents) and the tetrabutyl or tetrapentyl assumption for the transfer from methanol to NMP or DMSO (the tetraalkylammonium tetraalkylborate salts are concentration dependent in methanol, but reasonable extrapolations to $c = 0$ can be made). The sum of these two transfer values equals the enthalpy of transfer from methanol to DMF for the ion in question. A similar procedure may be used to obtain values from water to DMF, NEA, etc.

A second approach to the problem may be made based on the extrapolated values of tetraphenylarsonium chloride and the tetraalkylammonium tetraalkylborates in methanol. Using these values and the single ion enthalpies of transfer obtained from the tetraalkyl assumptions (methanol to a second solvent), it is possible to back-calculate the heat of solution of sodium tetraphenylborate in methanol. This procedure yields an average heat of solution for sodium tetraphenylborate in methanol of +1.3 kcal mole$^{-1}$ (the very crude extrapolation of experimental $\Delta H_s$ *vs.* concentration gives about 3.9 kcal mole$^{-1}$). Use of this calculated value in the tetraphenyl assumption gives results comparable with those obtained using the tetraalkyl assumptions.

Some recently reported[12] enthalpies of transfer (methanol to DMF) of transition states ($\Delta\Delta H^{t}$) for SN2 and SNAr reactions utilizes the expression $\Delta\Delta H^{t} = \Sigma\Delta\Delta H_s + \Delta\Delta H^{\ddagger}$, where $\Sigma\Delta\Delta H_s$ is the enthalpy of transfer of the reactants (the anion contribution to $\Sigma\Delta\Delta H_s$ is based on $\Delta\Delta H_s((C_4H_9)_4N^+) = \Delta\Delta H_s(^-B(C_4H_9)_4$ and $\Delta\Delta H^{\ddagger}$ is the difference in the enthalpies of activation of the reaction in the two solvents. For reactions such as displacement of iodide from methyl iodide by thiocyanate or *p*-nitrophenoxide and displacement

**Table III.** Enthalpies and Free Energies of Transfer from Methanol to DMSO at 25°

| Ion | $\Delta\Delta F$, kcal/g-ion[a,b] | $\Delta\Delta H_s$, kcal/g-ion |
|---|---|---|
| $Na^+$ | −4.9 | −3.4 |
| $K^+$ | −6.1 | −5.6 |
| $Cl^-$ | 7.2 | 6.6 |
| $Br^-$ | 4.6 | 2.3 |
| $I^-$ | 1.6 | −1.2 |
| $ClO_4^-$ | −0.4 | −1.9 |

[a] $\Delta\Delta F$ values from R. Alexander and A. J. Parker, *J. Amer. Chem. Soc.*, **89**, 5549 (1967). [b] Values based on tetraphenylarsonium tetraphenylborate assumption. Calculated from $\Delta\Delta F = 2.303RT\,{}^{m}\gamma^{s}$ (cal/g-ion).

of halide from a *p*-nitrohalobenzene by thiocyanate or azide, $\Delta\Delta H_s$ of the nucleophiles (protic to dipolar aprotic solvent) is not always the principal factor leading to the increased rate in the aprotic solvent. In fact, large polarizable nucleophiles may *gain* solvation by the transfer. In some cases, enhanced solvation of the transition state in the dipolar aprotic solvent is, by far, the more important factor. Our results for $\Delta H_s$ (at $c = 0$) for tetrabutylammonium tetrabutylborate in both methanol and DMF are quite different from the values at kinetic concentrations ($\Delta H_s = 6.99$ in methanol, $\Delta H_s = 5.97$ in DMF) previously reported,[12] although at high concentrations our values approach these. Recalculation of $\Delta\Delta H^{\ddagger}$ values using our values of $\Delta\Delta H_s$ ($Bu_4N^+$ and $^-BBu_4$) and the reported[12] $\Delta H_s$ values for reactants and substrates gives results which do not drastically change Haberfield's conclusions. However, it would be interesting to know $\Delta H^{\ddagger}$ and $\Delta H_s$ values at infinite dilution for the systems involved.

It appears that a gain in solvation of the transition state by the transfer from protic to dipolar aprotic solvent is an important factor in the observed rate increases. This would certainly play an important role in reactions using iodide or some other large, anionic nucleophile which gains in solvation in the transfer from protic to dipolar aprotic solvent. Conversely, in reactions with small anions and small substrates, the change in solvation of the anion appears to be the most important factor to consider.[16]

One may conclude from the present work that care should be exercised in choosing model ions for extrathermodynamic assumptions for the determination of single ion enthalpies of transfer. It may be wise to avoid solvents such as DMF and methanol when possible, and to make use of those solvents where little concentration dependency is found.

Comparison of the present work with that of Friedman[14] indicates that the ability of dipolar aprotic solvents to solvate the anions $ClO_4^-$, $I^-$, $Br^-$ and $Cl^-$ decreases in the order: DMF > propylene carbonate > DMSO >NMP. Further comparison of this work with that of Parker[16] shows that enthalpies of transfer do parallel free energies of transfer among the solvents discussed (with the exception of NEA for which no solubility data are available).

As shown in Table III, there is fair agreement between $\Delta\Delta H_s$ and $\Delta\Delta F$ values for the methanol to DMSO transfer. The trend (solvation increases with increasing size of anion) is the same for the methanol to DMF transfer, although the agreement between $\Delta\Delta H_s$ and $\Delta\Delta F$ is not as good.

## Experimental Section

**Reagents.** The alkali halides have been previously described.[15] Commercial tetraphenylarsonium chloride was vacuum dried at 100°.

*Anal.* Calcd for $C_{24}H_{20}AsCl$: Cl, 8.48. Found: Cl, 8.49.

The tetraalkylammonium halides, sodium perchlorate, and sodium tetraphenylborate were commercially available and were vacuum dried at 100–160°.

**Tetrabutylammonium Tetrabutylborate.** Tri-*n*-butylborane was synthesized by the method of Hurd[18] by the addition of 15 g (0.1 mol) of boron trifluoride etherate in ether to approximately 50 g (0.3 mol) of *n*-butylmagnesium bromide in ether at 5° under nitrogen. The mixture was treated with dilute hydrochloric acid, and the lower layer was washed twice with saturated sodium bicarbonate solution and twice with water, dried with magnesium sulfate, and filtered. The ether was evaporated and 8.1 g (44%) of tri-*n*-butylborane was distilled; bp 109° (17 mm). This was dissolved in *n*-pentane, and an excess of *n*-butyllithium in pentane was added. The colorless solid which precipitated (assumed to be lithium tetrabutylborate) ignited when exposed to the atmosphere, and all attempts to purify it failed. Instead, the solid was dissolved in water, and an excess of aqueous tetra-*n*-butylammonium bromide was added. The tetra-*n*-butylammonium tetra-*n*-butylborate which precipitated was recrystallized twice from isopropyl ether (from which peroxides had been removed by passage through alumina); mp 110.6–112.0°; yield <10%.

*Anal.* Calcd for $C_{32}H_{72}NB$: C, 79.86; H, 14.97. Found: C, 79.60; H, 14.69.

An impure commercial sample of the compound melted at 107.8–110.8° after repeated recrystallization from isopropyl ether and was not used.

**Tetrapentylammonium Tetrapentylborate.** Tri-*n*-pentylborane was prepared by passing diborane (generated from boron trifluoride etherate and sodium borohydride in diglyme) through a diglyme solution of 21.0 g (0.3 mol) of 1-pentene[19] at room temperature under nitrogen. After removal of diglyme under reduced pressure, 16 g (71% yield) of tri-*n*-pentylborane was distilled, bp 104° (3.5 mm). To the trialkylborane in pentane was added an ether–pentane solution of *n*-pentyllithium. The water extract of the reaction mixture was treated with an excess of aqueous tetra-*n*-pentylammonium chloride. The colorless tetra-*n*-pentylammonium tetra-*n*-pentylborate which precipitated was dried and recrystallized twice from isopropyl ether; mp 115.1–115.8°; yield 7.0 g (17%).

*Anal.* Calcd for $C_{40}H_{88}NB$: C, 80.90; H, 14.93. Found: C, 80.98; H, 14.93.

**Solvents.** The DMSO used was that previously reported.[15] DMSO was reused by distillation at 20 mm from 4A molecular sieves and collection over 4A molecular sieves. Karl Fischer (KF) titration of this distilled DMSO showed 10 ppm of water. Analysis of DMSO by gas chromatography (gc) showed 2–3 ppm of dimethyl sulfide. Reagent methanol was distilled from and collected over 3A molecular sieves. No impurities were detected by gc. KF titration showed 12 ppm of water. Reagent grade DMF was distilled from and collected over 4A molecular sieves before use. Gc showed no detectable quantity of dimethylamine (25 ppm was the minimum quantity detectable) or other volatile impurities. The water content was 6 ppm (KF titration). HMPT was distilled (bp 72° (0.75 mm)) from and collected over 13X molecular sieves. Gc showed no impurities. KF titration indicated 14 ppm of water. The NEA (Baker) as received was colored and contained substantial impurities. Three successive distillations (each from 4A molecular sieves) yielded a colorless liquid, bp 59–61 (0.4 mm). Gc showed no ethylamine, but two unknown peaks were present which were estimated to be less than 0.05% each. The water content (KF titration) was 2 ppm.

**Calorimetry.** The calorimetric procedure and apparatus have been previously described.[15]

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(18) D. T. Hurd, *J. Org. Chem.*, **13**, 711 (1948).

(19) Method of H. C. Brown, B. C. Subba Rao, and R. B. Wetherill, *ibid.*, **22**, 1136 (1957).