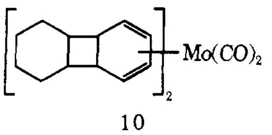
analogous to those previously described (**6** and **7**)



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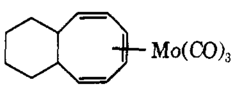

11

in the **1–2** system. The major difference is that now the yield of the $(diene)_2Mo(CO)_2$ complex **10** is small (~10%) while the yield of the triene complex **11** is much greater (~40%). This is consistent with the much higher relative stability of the triene **3** relative to the diene **4** as compared to the situation in the **1–2** system.

The two molybdenum carbonyl complexes have been structurally characterized by ir and pmr in much the same way as were the analogous compounds **6** and **7**. The $(diene)_2Mo(CO)_2$ complex has a pmr spectrum (Figure 6b) with the characteristic features of a coordinated 1,3-diene, and the triene complex **11** has a spectrum (Figure 8b) in the olefinic region very similar to that of cyclooctatrienemolybdenum tricarbonyl[12] and that of compound **7**.[16]

[16] NOTE ADDED IN PROOF. The crystal structures of **5** and **8** have been determined. The trans relationship of the fused rings postulated here for these compounds and their free olefin precursors, **2** and **4**, is thus confirmed. The conformation of the saturated 6-ring in **8** is intermediate between a chair and a half chair. Detailed reports on these structures are in preparation.

Solvation of Ions. XVII.[1] Free Energies, Heats, and Entropies of Transfer of Single Ions from Protic to Dipolar Aprotic Solvents

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Abstract: The results of applying several extrathermodynamic assumptions for estimating heats and entropies of transfer at 25° and free energies of transfer at 100° of single ions, when transferred from propylene carbonate to seven other solvents, are examined. With some exceptions, agreement between the assumptions is acceptable. We recommend that chemists adopt the assumptions that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$, $\Delta H_{tr}(Ph_4As^+) = \Delta H_{tr}(Ph_4B^-)$, and $\Delta S_{tr}(PhAs^+) = \Delta S_{tr}(Ph_4B^-)$.

The results of applying several extrathermodynamic assumptions, which are currently popular with chemists, for estimating single-ion free energies of transfer, ΔG_{tr}, from one solvent to another were compared in part XVI.[1] The comparisons were made in terms of solvent activity coefficients for transfer of a species i between a reference solvent 0 and another solvent S at 25°, and the thermodynamic relationships are as in eq 1.

$$\Delta G_{tr}(i) = 298R \ln {}^0\gamma_i{}^S \qquad (1)$$

Agreement between six quite different sets of assumptions was remarkably good, with a few reservations about one assumption when water was solvent. Thus we were able to recommend the assumption that there was negligible liquid junction potential in a cell composed of silver electrodes immersed in solutions of 0.01 *M* $AgClO_4$ in two solvents linked by a salt bridge of 0.1 *M* tetraethylammonium picrate in either solvent at 25°.

In this paper we examine the same extrathermodynamic assumptions, when applied to solutions at temperatures other than 25°, and also examine the results of applying these extrathermodynamic assumptions to enthalpies and entropies of transfer of single ions. Previous workers who have studied single ion enthalpies of transfer[3–6] have been almost unanimous in their choice of the assumption that $\Delta H_{tr}(Ph_4As^+) = \Delta H_{tr}(Ph_4B^-)$. Recent papers by Coetzee and Sharpe[7] and by Krishnan and Friedman[4] have shaken the confidence of those who favor this assumption. It is hoped that this paper will restore some of that confidence, at least when ΔH_{tr} is >5 kcal mol^{-1}.

We were by no means confident that the agreement noted in part XVI would extend from free energies to heats of transfer, because it is commonplace in chemistry to find that similar values of free energy result from widely differing but compensatory values of enthalpies and entropies. Clearly if chemists have confidence in values of ΔG_{tr}, ΔH_{tr}, and ΔS_{tr} for single ions, then they can obtain a much better understanding of ion–solvent interactions, within the framework of the assumption.

In this paper ΔG_{tr}, ΔH_{tr}, and ΔS_{tr} for transfer of both silver and bromide ions between eight solvents at 25 and 100° are estimated from four types of assumptions,[1] *i.e.*, the anion–molecule, the cation–molecule, the anion–cation, and the assumption of negligible liquid

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[1] Part XVI: R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Amer. Chem. Soc.*, **94**, 1148 (1972).

[2] Author to whom enquiries should be addressed.

[3] G. Choux and R. L. Benoit, *J. Amer. Chem. Soc.*, **91**, 6221 (1969).

[4] C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **75**, 3606 (1971).

[5] R. P. Held and C. M. Criss, *ibid.*, **71**, 2487 (1967).

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

[7] J. F. Coetzee and W. R. Sharp, *J. Phys. Chem.*, **75**, 3141 (1971).

Table I. Free Energy, ΔG_s, Enthalpy, ΔH_s (±0.2 kcal mol^{-1}), and Entropy, $-T\Delta S_s$, of Solution of AgBr and AgN_3 at 25° and Ionic Strength 0.011 *M* NBu_4ClO_4[a]

Solvent[b]	AgBr			AgN_3		
	ΔG_s^{298} [c]	ΔH_s	$-298\Delta S_s$[d]	ΔG_s^{298} [c]	ΔH_s	$-298\Delta S_s$[d]
DMSO	14.7	9.1	5.6	9.0	3.2	5.8
CH_3CN	18.0	9.3	8.7	13.5	6.4	7.1
DMF	20.8	11.8	9.0	15.4	8.0	7.4
H_2O	16.7	20.8	−4.1	11.7	16.9	−5.2
MeOH	21.1	18.0	3.1	15.6	12.0	3.6
TMS	25.4	20.3	5.1	20.2	16.4	3.8
PC	28.0	21.2	6.8	22.2	17.8	4.4
$MeNO_2$	29.8	19.0	10.8	23.9	17.0	6.9

[a] All values in kcal mol^{-1}. [b] Abbreviations are the following: DMSO, dimethyl sulfoxide; DMF, dimethylformamide; TMS, tetramethylene sulfone; PC, propylene carbonate. [c] Estimated as $-2.303RT \log K_s$, using values of the solubility product (in mol^2 $l.^{-2}$) at infinite dilution for these salts, as recorded in ref 1. [d] Calculated from $\Delta G_s^{266} = \Delta H_s - 298\Delta S_s$ at 25°.

junction potential in certain silver cells. A representative group of silver and bromide ion solvating solvents were selected to give a large spread of thermodynamic values.

At a later date we will discuss the significance of the numbers which follow from the assumptions, but it is not the purpose of this paper to consider the effect of ion–solvent interactions on ΔG_{tr}, ΔH_{tr}, and ΔS_{tr}, nor to discuss the different types of interaction which exist between ions and solvents. Our sole purpose at the moment is (i) to compare representative sets of data, based on a variety of extrathermodynamic assumptions, so as to generate confidence in three assumptions, *i.e.*, that $\Delta H_{tr}(Ph_4As^+) = \Delta H_{tr}(Ph_4B^-)$, that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$ at a number of temperatures, and that $\Delta S_{tr}(Ph_4As^+) = \Delta S_{tr}(Ph_4B^-)$, and (ii) to record values of ΔG_{tr} at different temperatures, ΔH_{tr}, and ΔS_{tr} for silver and bromide ions in a variety of solvents so as to establish reference points for single cations and anions, respectively.

Experimental Section

The purification of materials has been described previously[8] or was accomplished by standard methods of distillation or recrystallization. Heats of solution or precipitation were measured by conventional calorimetric methods using a Guild solution calorimeter equipped with a base line compensator and of a design essentially as described by Arnett and coworkers.[9] Electrochemical and kinetic measurements at different temperatures were made as previously described[1] for work at 25°.

The solubility of tetraphenylmethane was obtained by vpc analysis of saturated solutions using an SE-30 5% on Chromosorb W AW-DMCS column with triphenylmethane as an internal reference.

Results

Enthalpies of Solution. The enthalpies of solution ΔH_s of silver bromide and silver azide were obtained by measuring the heats of precipitation[10] of these salts from 0.01 *M* silver perchlorate and 0.001 *M* NBu_4Br or NBu_4N_3 at 23 ± 1°. No attempt has been made to convert ΔH_s at ionic strength 0.011 *M* to values at infinite dilution, it being assumed from related studies that the corrections are small for NBu_4^+ and ClO_4^- salts.[11] Table I lists the new enthalpies of solution ΔH_s, the previously reported free energies of solution[1] ΔG_s (*i.e.*, $-RT \ln K_s$ is the solubility product in mol^2 $l.^{-2}$ at zero ionic strength), and the entropies of solution ΔS_s (expressed as $-298\Delta S_s$) for AgBr and AgN_3. All values are in kcal mol^{-1} at 25°.

Temperature Dependence of the Emf of Silver Cells. The emf of cell A (ΔE) was measured at several different temperatures. The results are in Table II.

$$\text{Ag}\left|\begin{array}{c}\text{AgClO}_4\\ 0.01\,M\\ \text{solvent S1}\end{array}\right\|\begin{array}{c}\text{NEt}_4\text{Pic}\\ 0.1\,M\\ \text{S1 or S2}\end{array}\left\|\begin{array}{c}\text{AgClO}_4\\ 0.01\,M\\ \text{solvent S2}\end{array}\right|\text{Ag}$$

cell A

Table II. Emf of the Cell A at Various Temperatures

Solvent S1[a]	Solvent S2[a]	Emf, mV (temp, °C)
DMSO	PC[b]	560 (22.0), 558 (23.0), 567 (52), 566 (82.0)
CH_3CN	PC[b]	422 (0.0), 413 (23.0), 406 (55.0)
CH_3CN	MeOH[b]	273 (0.0), 272 (20.0), 267 (33.5), 264 (49.0)
DMSO	DMF[b]	197 (18.0), 197 (34.5), 194 (51.0)
CH_3CN	$MeNO_2$[b]	538 (0.0), 541 (56.0)
CH_3CN	TMS[b]	295 (32.0), 287 (47.5), 285 (60)
DMSO	TMS[b]	452 (29.0), 457 (37.0), 445 (57.0), 440 (84.0)
CH_3CN[b]	H_2O	206 (0.0), 156 (58.0)

[a] Abbreviations as in Table I. [b] This solvent was used in the bridge.

Pairs of solvents S1 and S2 were chosen to allow a temperature range of at least 50° for the measurements. The solvent used for the salt bridge was that which was the weaker solvator of silver cations of the pair. An exception was the cell involving acetonitrile and water, where the bridge solvent had to be acetonitrile because of the low solubility of NEt_4Pic in water.

The temperature dependence of ΔE gave ΔG, ΔH, and $-T\Delta S$ for the cell. The results in Table III were calculated from the relationship in (2), where ΔG, ΔH,

$$\Delta G_{cell} = \Delta H_{cell} - T\Delta S_{cell} = -\frac{F\Delta E_{cell}}{4.184 \times 10^3} \qquad (2)$$

and $-T\Delta S$ are in kcal/mol; *E* is in volts and *F* is in coulombs. Values of ΔE were obtained from Table II and all quantities are referred to acetonitrile as solvent S1 in cell A.

Temperature Dependence of the Oxidation of Ferrocene. Slow cyclic voltammetry on solutions of ferrocene at platinum using the procedure described in part

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(8) A. J. Parker and R. Alexander, *J. Amer. Chem. Soc.*, **90**, 3313 (1968).

(9) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).

(10) C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 3934 (1969).

(11) Y. C. Wu and H. L. Friedman, *ibid.*, **70**, 501 (1966).

Table III. Emf, ΔG, ΔH, and $-T\Delta S$ of Cell A at 25°[a]

Solvent S[b]	ΔE, V	ΔG_{cell},[c] kcal mol^{-1}	ΔH_{cell},[d] kcal mol^{-1}	$-298\Delta S_{\text{cell}}$,[d] kcal mol^{-1}
DMSO	−0.152	+3.5	+0.8	+2.7
DMF	0.040	−0.9	−4.5	+3.6
H_2O	0.185	−4.3	−10.2	+5.9
MeOH	0.270	−6.2	−7.8	+1.6
TMS[e]	0.300	−6.9	−11.7	+4.8
PC	0.414	−9.5	−11.2	+1.7
$MeNO_2$	0.538	−12.4	−12.7	+0.3

[a] Reference solvent acetonitrile. [b] Abbreviations as in Table I. [c] From eq 2. [d] Uncertainty is ±1.0 kcal/mol. [e] By extrapolation from 30°.

XVI[1] and a reference half-cell of Ag|$AgClO_4$ (0.01 *M*) in cell B gave values of E_1 (0.01 *M* Ag^+) − $E_{1/2}$ (ferrocene) at various temperatures. The results are listed in Table IV.

$$\text{Ag}\left|\begin{array}{c}\text{AgClO}_4\ \ 0.01\,M\\ \text{NEt}_4\text{ClO}_4\ \ 0.01\,M\\ \text{solvent S}\end{array}\right\|\begin{array}{c}\text{NEt}_4\text{ClO}_4\\ 0.1\,M\\ \text{solvent S}\end{array}\left\|\begin{array}{c}\text{ferrocene}\ \ 0.0002\,M\\ \text{NEt}_4\text{ClO}_4\ \ 0.02\,M\\ \text{solvent S}\end{array}\right|\text{Pt}$$

cell B

Table IV. Cyclic Voltammetry in Cell B

Solvent S[a]	E (0.01 *M* Ag^+) − $E_{1/2}$(ferrocene), mV[b] (temp, °C)
DMSO	−190 (25.0), −193 (52.0), −202 (82.0)
CH_3CN	−85 (0.0), −98 (34.0), −99 (60.0)
DMF	−14 (0.0), −8 (40.0)
H_2O	281 (0.0), 263 (56.0)
MeOH	148 (0.0), 144 (32.0)
TMS	241 (35.0), 233 (57.0), 238 (82.0)
PC	352 (20.0), 363 (46.0), 362 (85.0)
$MeNO_2$	452 (56.0), 450 (0.0)

[a] Abbreviations as in Table I. [b] Estimated uncertainty ±5 mV; temperature of measurement is in parentheses.

The temperature dependence of voltage of the ferrocene cell B gave values of ΔH_{cell} and $-T\Delta S_{\text{cell}}$ from eq 2, where $E_{\text{cell}} = E$ (0.01 *M* Ag^+) − $E^1/_2$ (ferrocene), as recorded in Table IV.

Values of E_{cell}, ΔG_{cell}, ΔH_{cell}, and $-T\Delta S_{\text{cell}}$ at 25° are listed in Table V.

Table V. Cyclic Voltammetry in Cell B at 25°

Solvent[a]	E_{cell}, mV	ΔG_{cell},[b] kcal mol^{-1}	ΔH_{cell},[c] kcal mol^{-1}	$-298\Delta S_{\text{cell}}$,[c] kcal mol^{-1}
DMSO	−190	+4.4	+3.1	+1.3
CH_3CN	−90	+2.1	+0.6	+1.5
DMF	−11	+0.3	+1.4	−1.1
H_2O	+272	−6.3	−8.5	−2.2
MeOH	145	−3.3	−4.1	+0.8
TMS[d]	237	−5.5	−6.2	+0.7
PC	357	−8.2	−7.0	−1.2
$MeNO_2$	452	−10.4	−10.5	+0.1

[a] Abbreviations as in Table I. [b] Calculated from eq 2. [c] Estimated uncertainty is ±1.0 kcal mol. [d] By extrapolation from 30°

Temperature Dependence of Solubility of Ph_4C. The solubilities, *S*, of tetraphenylmethane in different solvents at various temperatures are listed in Table VI.

Table VI. Solubility (10^3S)[b] of Tetraphenylmethane in Different Solvents[c]

Solvent[a]	Solubility
DMSO	0.77 (24.0), 2.4 (52.0), 8.0 (79.0)
CH_3CN	0.18 (4.0), 0.47 (24.0), 0.76 (34.0), 2.5 (59.0), 2.8 (65.0)
DMF	1.5 (4.0), 3.7 (30.0), 8.5 (52.0), 24.8 (79.0)
MeOH	0.11 (30.0), 0.15 (34.0), 0.53 (59.0), 0.78 (65.0)
TMS	2.0 (30.0), 5.2 (55.0), 16.5 (85.0)
PC	0.39 (4.0), 0.67 (24.0), 0.90 (34.0), 3.3 (62.0), 8.9 (85.0)

[a] Abbreviations as in Table I. [b] Solubility in mol l.$^{-1}$. [c] At temperature shown in parentheses (±0.5°).

Free energies, enthalpies, and entropies of solution of tetraphenylmethane in the various solvents were obtained from the values listed in Table VI using the standard equations $\Delta G_s = \Delta H_s - T\Delta S_s = -2.303RT \log S$. These values, together with the solubilities at 25°, are listed in Table VII.

Table VII. Thermodynamic Parameters for the Solution of Tetraphenylmethane in Various Solvents at 25°

Solvent[a]	−Log S[b]	ΔG_s,[c] kcal mol^{-1}	ΔH_s, kcal mol^{-1}	$-298\Delta S_s$, kcal mol^{-1}
DMSO	3.1	4.2	8.4	−4.2
CH_3CN	3.3	4.5	8.5	−4.0
DMF	2.5	3.4	7.7	−4.3
MeOH	4.1	5.6	10.8	−5.2
TMS	2.8	3.8	8.3	−4.5
PC	3.1	4.2	7.2	−3.0

[a] Abbreviations as in Table I. [b] S is the solubility of tetraphenylmethane in mol l.$^{-1}$. [c] From $\Delta G_s = -2.303RT \log S$.

Discussion

Enthalpies of Transfer. Using the results presented in Tables I–VII, together with measured heats of solution of various electrolytes taken from the literature, it is possible to obtain single-ion enthalpies and entropies of transfer of Ag^+ and Br^-, according to six different assumptions, as shown below. In all cases, propylene carbonate (PC) has been chosen as the reference solvent. Apart from water, and following the work of Friedman and coworkers,[4] the most comprehensive and consistent set of heats of solution is available for this solvent. Appropriate manipulations can give data referred to other solvents as reference.

The reasons underlying the choice of assumptions for free energies of transfer have been discussed previously;[1] the same reasons lead us to choose these assumptions for enthalpies and entropies of transfer.

Group 1. Anion–Cation Assumption. $\Delta H_{\text{tr}}(Ph_4As^+) = \Delta H_{\text{tr}}(BPh_4^-)$. Data tabulated by Choux and Benoit[3] for water, tetramethylene sulfone (TMS), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), methanol, and propylene carbonate (PC) and by Krishnan and Friedman[4] for DMF, MeOH, and PC give values of $\Delta H_{\text{tr}}(Br^-)$ for transfer from propylene carbonate, based on the assumption that $\Delta H_{\text{tr}}(Ph_4As^+) = \Delta H_{\text{tr}}(BPh_4^-)$. By combining these results with those given in Table I for the heats of solution of AgBr, it is then possible to obtain $\Delta H_{\text{tr}}(Ag^+)$ using eq 3.

$$\Delta H_{\text{tr}}(Ag^+) = \Delta H_{\text{tr}}(AgBr) - \Delta H_{\text{tr}}(Br^-) \qquad (3)$$

For solvents other than methanol and DMF, heats of solution of various electrolytes found by different workers agree very well. However for a number of electrolytes in methanol, particularly tetraphenylarsonium and tetraphenylboride salts and sodium tetraphenylboride in DMF for which values of −12.2,[3] −19.8,[5] and −17.3[4] kcal mol^{-1} have been obtained, there are some large discrepancies. In some cases these differences arose from an apparent temperature dependence of the heat of solution of some electrolytes at very low concentrations ($<2 \times 10^{-4}$ *M*) in methanol and DMF.[5] Recently Krishnan and Friedman[4] have made a very careful study of the heats of solution of a number of electrolytes in methanol and DMF and have obtained an internally consistent set of data, thus removing many of the previous anomalies. We have chosen their data in preference to earlier work, where any differences arise.

Group 2. Cation–Molecule. (a) **ΔH_{tr}(Ferrocene) = ΔH_{tr}(Ferricinium).** Table V lists the values of E_{cell}, ΔG_{cell}, ΔH_{cell}, and $-T\Delta S_{cell}$ at 25° obtained from cyclic voltammetry in cell B in different solvents at various temperatures. Following the well-known Strehlow[12] assumption for free energies of transfer, if it is assumed that ΔH_{tr}(ferrocene) = ΔH_{tr}(ferricinium), then values of $\Delta H_{tr}(Ag^+)$ follow from eq 4. $\Delta H_{tr}(Br^-)$

$$\Delta H_{tr}(Ag^+) = \Delta H(\text{cell}^s) - \Delta H(\text{cell}^{PC}) \qquad (4)$$

then follows from eq 5.

$$\Delta H_{tr}(Br^-) = \Delta H_{tr}(AgBr) - \Delta H_{tr}(Ag^+) \qquad (5)$$

Results were obtained for transfer from propylene carbonate to the following solvents: H_2O, TMS, DMF, DMSO, MeOH, CH_3CN, $MeNO_2$.

(b) **$\Delta H_{tr}(Ph_4As^+) = \Delta H_{tr}(Ph_4C)$.** Following the Grunwald, Baugham, and Kohnstam[13] assumption for free energies of transfer, if one assumes that $\Delta H_{tr}(Ph_4As^+) = \Delta H_{tr}(Ph_4C)$, then $\Delta H_{tr}(Br^-)$ can be obtained from eq 6, using enthalpies of solution measured

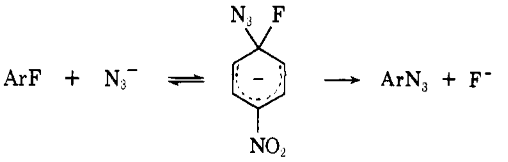
$$\Delta H_{tr}(Br^-) = \Delta H_{tr}(Ph_4AsBr) - \Delta H_{tr}(Ph_4C) \qquad (6)$$

by others for Ph_4AsBr in various solvents,[10] plus our enthalpy of solution of Ph_4AsBr in acetonitrile (1.90 ± 0.02 kcal mol^{-1}) together with $\Delta H_s(Ph_4C)$ obtained from Table VII. Where enthalpies for Ph_4AsBr were not available (*i.e.*, DMF, MeOH, TMS), ΔH_s for Ph_4AsCl[4] were used with the difference between $\Delta H_{tr}(Br^-)$ and $\Delta H_{tr}(Cl^-)$ (independent of any assumption) using the tabulations of Choux and Benoit[3] and Krishnan and Friedman.[4] Values of $\Delta H_{tr}(Ag^+)$ were obtained from eq 3 and the appropriate data.

Group 3. Anion–Molecule Assumption. (a) **$\Delta H_{tr}(BPh_4^-) = \Delta H_{tr}(Ph_4C)$.** From the data of Choux and Benoit[3] for several solvents and of Krishnan and Friedman[4] for MeOH and DMF, it is possible to obtain values of $\Delta H_{tr}(Br^-) - \Delta H_{tr}(BPh_4^-)$ for transfer from propylene carbonate to H_2O, MeOH, DMF, DMSO, and TMS. This difference is independent of any assumption. Following Grunwald, Baugham, and Kohnstam's[13] assumption for free energies of transfer, if it is assumed that $\Delta H_{tr}(Ph_4C) = \Delta H_{tr}(BPh_4^-)$, then $\Delta H_{tr}(Br^-)$ follows from eq 7. Values of $\Delta H_{tr}(Ag^+)$ were again obtained from eq 3.

$$\Delta H_{tr}(Br^-) = \Delta H_{tr}(Br^-) - \Delta H_{tr}(BPh_4^-) + \Delta H_{tr}(Ph_4C) \qquad (7)$$

(b) **$\Delta H_{tr}(ArF) = \Delta H_{tr}(\ddagger^-)$.** The bimolecular aromatic nucleophilic reactions of 4-fluoronitrobenzene (ArF) with azide ions (eq 8) pass through a transition-


(8)

I

$(Ar = 4\text{-}NO_2C_6H_4)$

state anion resembling structure I and denoted by ($\ddagger^-$) in eq 9.

$$\Delta H^{\ddagger}(PC) - \Delta H^{\ddagger}(S) = \Delta H_{tr}(\ddagger^-) - \Delta H_{tr}(ArF) - \Delta H_{tr}(N_3^-) \qquad (9)$$

Equation 9 follows from transition-state theory, where $\Delta H^{\ddagger}(PC)$ and $\Delta H^{\ddagger}(S)$ represent the enthalpy of activation of reaction 8 in propylene carbonate and solvent S, respectively. Following Parker's assumption[1] for free energies of activation, for reactions of this type, if it is assumed that $\Delta H_{tr}(\ddagger^-) = \Delta H_{tr}(ArF)$, then $\Delta H_{tr}(N_3^-)$ follows from eq 10. Using published values

$$\Delta H_{tr}(N_3^-) = \Delta H^{\ddagger}(S) - \Delta H^{\ddagger}(PC) \qquad (10)$$

of the enthalpy of activation of reaction[14] (Table VIII), together with measured heats of solution of AgN_3 from Table I, it is possible to obtain values of $\Delta H_{tr}(Ag^+)$ by use of eq 10 and 11. Values of $\Delta H_{tr}(Br^-)$ can then be

$$\Delta H_{tr}(Ag^+) = \Delta H_{tr}(AgN_3) - \Delta H_{tr}(N_3^-) \qquad (11)$$

obtained from eq 3.

Table VIII. Values of $\Delta H^{\ddagger}$ for Reaction 8

Solvent[a]	$\Delta H^{\ddagger}$,[b,c] kcal mol^{-1}	Solvent[a]	$\Delta H^{\ddagger}$,[b,c] kcal mol^{-1}
DMSO	18.7	MeOH[d]	23.6
CH_3CN	17.1	TMS	15.9
DMF[d]	18.5	PC	15.7
H_2O	24.1	$MeNO_2$	18.6

[a] Abbreviations as in Table I. [b] Enthalpy of activation of reaction 8. [c] From ref 14. [d] J. Miller and A. J. Parker, *J. Amer. Chem. Soc.*, **83**, 117 (1961).

Group 4. Negligible E_{lj}. Following Parker's assumption[1] for free energies of transfer, if it is assumed that there is negligible liquid junction potential in cell A, then eq 12 follows where PC (propylene carbonate) is

$$\Delta H_{tr}(Ag^+) = -{}^{PC}\Delta H^{s}_{cell} \qquad (12)$$

one of the two solvents in cell A.

Values of ${}^{PC}\Delta H^{s}_{cell}$ can be obtained from the data in Table III by subtracting ${}^{MeCN}\Delta H^{PC}_{cell}$ (= 11.2 kcal mol^{-1}) from the other values of ${}^{MeCN}\Delta H^{s}_{cell}$. $\Delta H_{tr}(Br^-)$ for transfer from propylene carbonate is again obtained from eq 3.

Entropies of Transfer. Using the methods outlined, it is possible to obtain values of $\Delta H_{tr}(Ag^+)$ and $\Delta H_{tr}(Br^-)$ for transfer from propylene carbonate according to six different assumptions from the four groups listed above. By combining these values with previously

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(12) H Strehlow and H. M. Koepp, *Z. Elektrochem.*, **62**, 373 (1958)'

(13) E. Grunwald, G. Baugham, and G. Kohnstam, *J. Amer. Chem. Soc.*, **82**, 5801 (1960).

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Table IX. Free Energies, Enthalpies, and Entropies of Transfer of Ag^+ from Propylene Carbonate (kcal/mol at 25°)[a]

Solvent		Group 1 $Ph_4As^+ = BPh_4^-$	Group 2A $F^+ = F$	Group 2B $Ph_4As^+ = Ph_4C$	Group 3A $Ph_4B^- = Ph_4C$	Group 3B $ArF = (\mp^-)$	Group 4 negligible E_{1j}
DMSO	ΔG	−11.9[b]	−12.6	−12.0[b]	−11.0[b]	−13.1	−13.0
	ΔH	−8.9	−10.1	−9.1	−8.7	−11.6	−12.0
	$-T\Delta S$	−2.2	−2.5	−2.9	−2.3	−1.5	−1.0
CH_3CN	ΔG	−8.0	−10.1	−9.8	−7.5	−8.3	−9.5
	ΔH		−7.6	−8.4		−10.0	−11.2
	$-T\Delta S$		−2.5	−1.4		+1.7	+1.7
DMF	ΔG	−7.2	−8.7	−7.6	−6.9	−7.4	−8.6
	ΔH	−7.1	−8.4	−5.4	−8.8	−7.0	−6.7
	$-T\Delta S$	−0.1	−0.3	−2.2	+1.9	−0.4	−1.9
H_2O	ΔG	+2.8[b]	−1.9			−4.1	−5.2
	ΔH	+4.0	+1.5			+7.0	−1.0
	$-T\Delta S$	−6.8[b]	−3.4			−11.1	−4.2
MeOH	ΔG	−0.8	−4.9	−2.5	+0.6[b]	−0.8	−3.3
	ΔH	−1.1	−2.9	+0.4	−1.7	+2.1	−3.4
	$-T\Delta S$	+0.3	−2.0	−2.9	+2.3	−2.9	+0.1
TMS	ΔG	−4.0	−2.5	−4.1	−3.1	−2.6	−2.6
	ΔH	+0.1	−0.8	+1.3	−1.3	−1.2	+0.5
	$-T\Delta S$	−4.1	−1.7	−5.4	−1.8	−1.4	−3.1
PC	ΔG	0.0	0.0	0.0	0.0	0.0	0.0
	ΔH	0.0	0.0	0.0	0.0	0.0	0.0
	$-T\Delta S$	0.0	0.0	0.0	0.0	0.0	0.0
$MeNO_2$	ΔG	+3.0	+2.2	+2.2	+3.1	+2.6	+2.9
	ΔH		+3.5			+2.1	+1.5
	$-T\Delta S$		−1.3			+0.5	+1.4

[a] Values calculated from ref 1. [b] Value calculated from I. M. Kolthoff and M. K. Chantooni, *J. Phys. Chem.*, **76**, 2024 (1972).

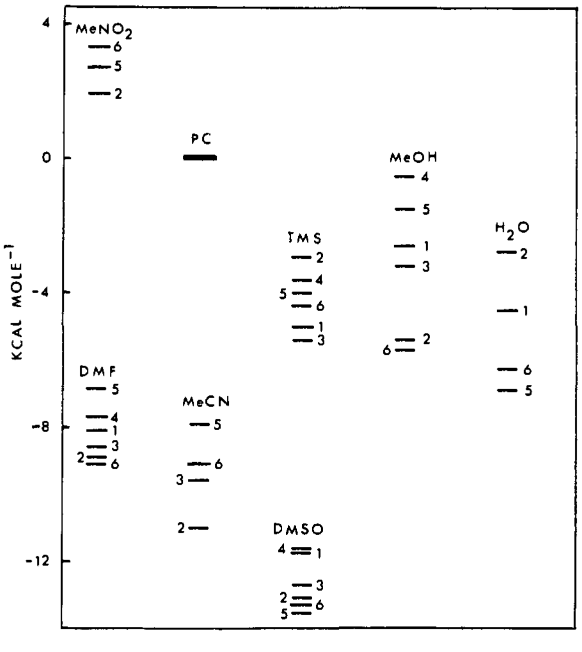

Figure 1. Free energies of transfer of Ag^+ from reference solvent propylene carbonate (PC) to other solvents at 100° using the following extrathermodynamic assumptions: 1, $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(BPh_4^-)$; 2, $\Delta G_{tr}(Fe(C_5H_5)_2) = \Delta G_{tr}(Fe(C_5H_5)_2^+)$; 3, $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4C)$; 4, $\Delta G_{tr}(Ph_4C) = \Delta G_{tr}(BPh_4^-)$; 5, $\Delta G_{tr}(ArF) = \Delta G_{tr}(ArN_3F(\mp^-))$; 6, negligible E_{1j}. DMSO is dimethyl sulfoxide, DMF is dimethylformamide, TMS is tetramethylene sulfone, and Ar is $4\text{-}NO_2C_6H_4$.

published values of ΔG_{tr} for these ions,[1] values of $-T\Delta S_{tr}$ can then be obtained. Values of ΔG_{tr}, ΔH_{tr}, and $-T\Delta S$, with T = 298, for Ag^+ and Br^- are listed in Tables IX and X. Figure 1 shows a comparison of $\Delta G_{tr}(Ag^+)$ according to the various assumptions at 25 and 100°. The values at 100° have been obtained from eq 13, by assuming that $\Delta H_{tr}(Ag^+)$ and $\Delta S(_{tr}Ag^+)$

$$\Delta G_{tr}(Ag^+)\,(100°) = \Delta H_{tr}(Ag^+) - 373\Delta S_{tr}(Ag^+) \quad (13)$$

are independent of temperature over this range.

The conclusions to be derived from this work are the following. (1) The extrathermodynamic assumptions used to derive free energies of transfer of silver cation from propylene carbonate to other solvents at 25° are equally acceptable when applied to transfers at 100°. This is apparent from Figure 1. The ferrocene assumption for transfer to water and methanol at 100° provides the most apparent anomaly, just as was found for solutions at 25°. (2) The same extrathermodynamic assumptions, if used to derive enthalpies and entropies of transfer, although producing greater scatter than found with free energies of transfer, produce much the same result, no matter which assumption is used. Some glaring anomalies are found between all assumptions for transfer to water, with the kinetic assumption for transfer to methanol[14] and with the cation-molecule assumption for transfer to DMF. The failure of the kinetic assumption for transfer to methanol surprises us, and we cannot account for it. This is unfortunate because methanol occupies an important position as a solvent for SNAr reactions.[15]

In the evaluation, it should be appreciated that the measurements in cell A and B lead to values of ΔH_{tr} and ΔS_{tr} which are subject to uncertainties of ±1 kcal mol^{-1}, whereas other assumptions provide values of uncertainty $< \pm 0.3$ kcal mol^{-1}.

Choice of Assumption for ΔH_{tr} and ΔS_{tr}. The measurements of the voltages of cell A and cell B at different temperatures cannot be sufficiently precise to allow experimental values of ΔH_{tr} of satisfactory precision, so we cannot recommend our assumption[1] of negligible E_{1j} for ΔH_{tr}. The ferrocene assumption is suspect for

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(15) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

Table X. Free Energies,[b] Enthalpies, and Entropies of Transfer of Br^- from Propylene Carbonate (kcal mol^{-1} at 25°)

Solvent[a]		Group 1 $Ph_4As^+ = Ph_4B^-$	Group 2A $F^+ = F$	Group 2B $Ph_4As^+ = Ph_4C$	Group 3A $Ph_4B^- = Ph_4C$	Group 3B ArF = $(\pm^-)$	Group 4 negligible E_{lj}
DMSO	ΔG	−2.1	−0.7	−1.3	−2.3	−0.2	−0.3
	ΔH	−3.2	−2.0	−3.0	−3.4	−0.5	−0.1
	$-T\Delta S$	+1.1	+1.3	+1.7	+1.1	+0.3	−0.2
CH_3CN	ΔG	−2.0	+0.3	−0.2	−2.5	−1.7	−0.5
	ΔH		−4.3	−3.5		−1.9	−0.7
	$-T\Delta S$		+4.6	+3.3		+0.2	+0.2
DMF	ΔG	0.0	+1.5	+0.4	−0.3	+0.2	+1.4
	ΔH	−2.3	−1.0	−4.0	−0.6	−2.4	−2.7
	$-T\Delta S$	+2.3	+2.5	+4.4	+0.3	+2.6	+4.1
H_2O	ΔG	−8.4	−9.4			−7.2	−6.1
	ΔH	−4.4	−1.9			−7.4	+0.6
	$-T\Delta S$	−4.0	−7.5			+0.2	−6.7
MeOH	ΔG	−6.1	−2.0	−4.4	−7.5	−6.1	−3.6
	ΔH	−2.1	−0.3	−3.0	−1.5	−5.1	+0.2
	$-T\Delta S$	−4.0	−1.7	−1.4	−6.0	−1.0	−3.8
TMS	ΔG	+1.4	−0.1	+1.5	+0.5	0.0	0.0
	ΔH	−1.0	−0.1	−2.2	+0.4	+0.3	−1.4
	$-T\Delta S$	+2.4	0.0	+3.7	+0.1	−0.3	+1.4
PC	ΔG	0.0	0.0	0.0	0.0	0.0	0.0
	ΔH	0.0	0.0	0.0	0.0	0.0	0.0
	$-T\Delta S$	0.0	0.0	0.0	0.0	0.0	0.0
$MeNO_2$	ΔG	−1.2	−0.4	−0.4	−1.3	−0.8	−1.1
	ΔH		+5.1			+3.4	+2.6
	$-T\Delta S$		−5.5			−4.2	−3.7

[a] Abbreviations as in Table I. [b] Calculated from data in Table IX and ref 1 *via* the equation $\Delta G_{tr}(Br^-) = \Delta G_{tr}(AgBr) - \Delta G_{tr}(Ag^+)$.

transfer to water. Thus the choice reduces to $\Delta H_{tr}(Ph_4As^+) = \Delta H_{tr}(Ph_4B^-)$, $\Delta H_{tr}(Ph_4As^+) = \Delta H_{tr}(Ph_4C)$, $\Delta H_{tr}(Ph_4B^-) = \Delta H_{tr}(Ph_4C)$, or $\Delta H_{tr}(\pm^-) = \Delta H_{tr}(ArF)$. In view of the already wide use of the tetraphenylarsonium tetraphenylboride assumption for estimating ΔH_{tr}, the difficulties with slightly soluble tetraphenylmethane, the less fundamental kinetic assumption, and the increasing confidence[1] in the first assumption for ΔG_{tr}, we recommend that chemists adopt the assumptions that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$ at all temperatures, that $\Delta H_{tr}(Ph_4As^+) = \Delta H_{tr}(Ph_4B^-)$ and $\Delta S_{tr}(Ph_4As^+) = \Delta S_{tr}(Ph_4B^-)$.

The fact that a variety of assumptions give reasonable agreement to within ±1 kcal mol^{-1} encourages us to believe that real *energies* and entropies of transfer of single ions (despite differences for interaction of Ph_4As^+ *vs.* Ph_4B^- as revealed by spectroscopic methods, *e.g.*, nmr[7]) are reproduced to within ±1 kcal mol^{-1} by the $Ph_4As^+ = Ph_4B^-$ assumption. If, for example, Ph_4B^- had a specific interaction with water as revealed by spectrometric methods, which was large in *energy* terms and was not present in aqueous solutions of Ph_4C, Ph_4As^+, ferrocene, liquid junctions, and so on, then the agreement shown in Tables IX and X would not exist. We will never know if an assumption is "correct" or not, so, for reasons given in part XVI,[1] we see little point, given the historical position occupied by $Ph_4As^+ = Ph_4B^-$, in chemists continuing to seek "better" assumptions and trying to destroy confidence in this assumption. Provided that reproducible and accurate numbers can be obtained from $Ph_4As^+ = Ph_4B^-$ then these numbers will be much more useful to chemists than would a variety of sets of numbers, based on each author's pet assumption. Most chemists probably feel that this assumption is "real" to within ±1 kcal mol^{-1}, so that if one is considering big explanations for big ion-solvent interactions, the assumption is acceptable. If an interaction produces only a small effect of 1 kcal mol^{-1} or so, then it is only worth a small "real" explanation anyway, and doubts as to the "real" precision of $Ph_4As^+ = Ph_4B^-$ will only concern a few chemists. Even for these small interactions, *differences* between ions of 0.1 kcal mol^{-1} are revealed and are meaningful, although real single ion values are uncertain.

We also note that values of ΔG_{tr} for silver cation are virtually the same, whether one uses the $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$ assumption, or the assumption of negligible liquid junction potential in cell A. The latter is an easier, more convenient, and more precise measurement to make so our recommendation in part XVI[1] still stands as a secondary assumption.

Our final point at this time, prior to a full discussion of ΔG_{tr}, ΔH_{tr}, and ΔS_{tr} for single ions, is that with the exception of transfer to or from water, values of $T\Delta S_{tr}$ for Ag^+ or Br^- are small, even when ΔG_{tr} of Ag^+ or Br^- are large. In other words, except when water is the solvent, changes in the free energy of ions with solvent transfer are reflected much more in the enthalpy rather than the entropy of transfer. The very negative values of $-T\Delta S_{tr}$ for transfer of Ag^+ and Br^- from propylene carbonate to water are consistent with substantial structure breaking by these ions in water or to substantial structure making by these ions in propylene carbonate.