also successfully calculated the bond angles in ClF_3 using a basis set of s and p orbitals only. Thus it appears, according to empirical molecular orbital theories, that the role of the 3d orbitals is to stabilize the second-row molecule,[8] rather than to be an essential factor in determining the molecular shape (which appears to be largely determined by the s and p orbitals).

Conclusions

The original method proposed for the derivation of the atomic parameters $^1/_2(I + A)$ in the CNDO theory was based on atomic spectral data.[5] An attempt was made to follow this method when the theory was extended to include second-row atoms,[8] but the paucity of data resulted in many uncertainties in the parameters which were obtained. In principle there is no reason why these parameters should not be obtained independently of spectral data, as are the off-diagonal parameters, by a comparison of the CNDO molecular orbitals with some reference calculation. This procedure has been investigated in the present paper.

Although the calibration method proposed above is in principle as good as any other, the present calculations suggest that it leaves something to be desired. This is because the molecular orbitals were found to be more sensitive to changes in the ratio of the diagonal to the off-diagonal parameters than to individual changes in these quantities. Nevertheless, some improvement in the second-row parameters has been obtained.

The calculations based on the revised parameters give reliably better dipole moments than the original calculations,[8] but there is a slight deterioration in the theoretical bond angles. However, qualitatively the two calculations are very similar and lead to the same general conclusions concerning the importance of 3d orbitals to the bonding of second-row atoms.

Attempts to generalize the method further to include atoms in other rows of the periodic table will face even more serious difficulties as regards the availability of atomic spectral data. As we have found that it is not completely satisfactory to base the parametrization solely on a comparison with a reference calculation, the most fruitful approach will probably be to make use of experimental data, such as dipole moments.

Solvation of Ions. XIII.[1] Solvent Activity Coefficients of Ions in Protic and Dipolar Aprotic Solvents. A Comparison of Extrathermodynamic Assumptions

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Abstract: Some extrathermodynamic assumptions for estimating single-ion solvent activity coefficients in water, formamide, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, acetonitrile, hexamethylphosphoramide, nitromethane, N-methyl-2-pyrrolidone, and 80% v/v DMSO–methanol at 25° and sulfolane at 30° are compared. We estimate that values of log ${}^{M}\gamma^{S}_{Ag^+}$ for transfer of silver cation from methanol to other solvents, S, are -0.8 (H_2O), -3.7 ($HCONH_2$), -5.1 (DMF), -6.6 (DMAC), -8.2 (DMSO), -6.3 (CH_3CN), -10 (HMPT), 1.7 (CH_3NO_2), -2 (sulfolane), -6.8 (NMePy), -7.4 (DMSO-M). Liquid junction potentials between Ag|$AgNO_3$ half-cells linked by a bridge of saturated tetraethylammonium picrate in these solvents have been evaluated. The iodine–triiodide assumption is, in our opinion, one of the easiest of the acceptable extrathermodynamic assumptions to apply to new solvent systems.

The question of single-ion solvent activity coefficients ${}^{0}\gamma^{S}_{A^+}$ and ${}^{0}\gamma^{S}_{B^-}$ for transfer of cations, A^+, or of anions, B^-, from a reference solvent (superscript 0) to another solvent (superscript S) and the extrathermodynamic assumptions needed to split ${}^{0}\gamma^{S}_{A^+}$ and ${}^{0}\gamma^{S}_{B^-}$ are topics of great importance and current interest.[1,3-18] There is even greater interest for us when one of the solvents is protic and the other is dipolar aprotic.[12,15,18] We will never know if an assumption is valid,[3] but the greater the number of independent assumptions, leading to similar values, the greater our confidence in those values. For this reason, a noncritical comparison of

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Table I. Formal Solubility Products (Molar Concentrations) of Electrolytes Expressed as Solvent Activity Coefficients at 25°[a]

Solute AB	pK MeOH	Log $^{M}\gamma^{S}{}_{A^+}{}^{M}\gamma^{S}{}_{B^-}$ = pK(S) − pK(M)[b] in the solvent											
		MeOH	H_2O	$HCONH_2$	DMF	DMAC	DMSO	CH_3CN	HMPT	CH_3NO_2	TMS[e]	NMePy	80 DMSO-M
Ph_4C	3.7[d] ±0.1	0.0	...	...	−1.6[d] ±0.2	−1.4[d] ±0.2	...	−0.5[d] ±0.2	...	...	...	...	...
Ph_4Sn	3.6[d] ±0.1	0.0	...	...	−1.6[d] ±0.2	...	...	...	...	...	...	...	...
Ph_4AsBPh_4	9.0[c] ±0.1	0.0	8.2 ±0.6	−0.1[c] ±0.2	−5.3[c] ±0.2	−5.3[c] ±0.2	−5.4[c] ±0.2	−3.3[c] ±0.2	−5.3[c]	...	−4.0[c,e] ±0.2	...	...
Ph_4AsPic	3.6 ±0.1	0.0	5.2 ±0.2	...	...	...	...	−1.5 ±0.3	...	...	...	...	...
Ph_4AsI	1.6 ±0.2	0.0	3.7 ±0.4	0.3 ±0.4	−0.3 ±0.4	...	...	0.6 ±0.3	...	...	...	...	...
Ph_4AsClO_4	4.7 ±0.1	0.0	3.5 ±0.2	...	...	...	...	....	...	..	...	...	...
Ph_4AsSCN	1.4 ±0.3	0.0	4.4 ±0.4	...	...	...	...	...	...	...	...	...	...
KCl	2.6 ±0.2	0.0	−3.4 ±0.4	−2.6[c] ±0.4	2.9 ±0.3	...	0.6[f]	4.7 ±0.3	...	...	...	...	...
$KBPh_4$	5.0 ±0.1	0.0	2.5 ±0.3	−2.2[c] ±0.3	...	...	...	−2.6[c] ±0.3	...	...	...	...	...
KPic	4.2 ±0.1	0.0	−0.8 ±0.1	...	−4.4 ±0.4	...	...	+0.3 ±0.2	...	...	...	...	...
$KClO_4$	4.5 ±0.1	0.0	−2.8 ±0.1	...	−4.4 ±0.4	...	...	...	...	...	...	...	...
AgCl	13.1 ±0.1	0.0	−3.3 ±0.1	−3.7 ±0.2	1.4 ±0.2	1.2 ±0.2	−2.7 ±0.2	−0.2 ±0.2	−1.2 ±0.2	6.7[c] ±0.3	3.8[c,e] ±0.3	1.3[c] ±0.3	−3.2[c] ±0.2
$AgBPh_4$	13.9 ±0.3	0.0	−2.8 ±0.4	−3.6 ±0.3	−7.2 ±0.3	−8.0 ±0.3	−9.3 ±0.3	−6.7 ±0.3	−9.2 ±0.3	... ...	−4.4[c,e] ±0.3	...	...
AgPic	2.9 ±0.1	0.0	−0.2 ±0.2	...	...	...	...	...	...	...	...	...	...
AgI	18.3 ±0.1	0.0	−2.3 ±0.1	−3.8 +0.3	−2.5 ±0.2	−3.6 ±0.2	−6.9 ±0.3	−4.1 ±0.3	...	4.3[c] ±0.3	0.4[c,e] ±0.2	−3.8[c] ±0.3	−5.9[c] ±0.2
AgSCN	13.9 ±0.1	0.0	−2.0 ±0.1	−4.0 ±0.2	−2.4 ±0.2	−3.4 ±0.2	−6.8 ±0.2	−3.9 ±0.2	−6.5 ±0.2	4.1[c] ±0.2	0.6[c,e] ±0.2	−3.9[c] ±0.2	−5.8[c] ±0.2
AgN_3	11.2 ±0.1	0.0	−2.6 ±0.1	−3.5 ±0.2	−0.2 ±0.2	−0.4 ±0.2	−4.7 ±0.2	−1.6 ±0.2	−2.7 ±0.2	6.3[c] ±0.2	3.4[c,e] ±0.2	−0.5[c] ±0.2	...
AgBr	15.2 ±0.1	0.0	−2.9 ±0.1	−3.8 ±0.2	−0.2 ±0.2	−0.7 ±0.2	−4.6 ±0.2	−2.3 ±0.2	−2.9 ±0.2	...	...	...	...

[a] Reference solvent: methanol. Results are from ref 1 or 17 unless stated otherwise, but estimated limits of uncertainty have been reduced in the present table, following additional measurements. [b] The solubility products (mole^2 l.$^{-2}$) are usually measured to within ±0.1 log unit and can be reproduced as such by algebraic manipulation of this table. Since log $^{M}\gamma^{S}{}_{A^+}{}^{M}\gamma^{S}{}_{B^-}$ is a difference of two solubility products, the values shown are ±0.2 or greater. [c] This work. [d] These are solubilities in mole l.$^{-1}$ recorded as log S and log S(M) − log S(S) = log $^{M}\gamma_{i}{}^{S}$. [e] At 30.0°. [f] J. N. Butler, *J. Electroanal. Chem.*, **14**, 89 (1967).

some assumptions, imperfect as most are, may be helpful at this time.

We have calculated solvent activity coefficients,[3,12,17] log $^{M}\gamma^{S}{}_{Ag^+}$, for transfer of the silver cation from the reference solvent, methanol (M), to water, formamide, dimethylformamide (DMF), 80% v/v DMSO–methanol (80 DMSO-M), dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), acetonitrile, hexamethylphosphoramide (HMPT), nitromethane, and N-methyl-2-pyrrolidone (NMePy) at 25° and to sulfolane (TMS) at 30°, in terms of 16 extrathermodynamic assumptions, suggested by us and other workers.

Only those assumptions which are not adequately covered in the literature are outlined. Because we do not wish to justify any one assumption or say at this time that one has greater validity than another, the discussion has been kept to a minimum.

All rate and equilibrium constants and solubilities are concentration quotients on the molar scale at 25°. Though aware of the molal and mole fraction scales,[3,8] the molar scale is more useful for our purposes. The three are easily interconverted.[3] Debye–Hückel corrections[8] for "salt" activity coefficients in each solvent of similar dielectric constant have not been made. In many cases our reference solvent and the other solvent, of similar dielectric constant, are in fact 0.1–0.005 M in electrolyte rather than at infinite dilution, but similar corrections would be made to each solvent, and we are concerned with differences. Ion association may occasionally be greater than the small allowance we have made for it. Sometimes we have only had ion association constants for related electrolytes. Our solubility relationships[1,17] are subject to the usual assumption that the solid phase is the same, *or has comparable free energy*, in all solvents. We suspect that this is not a valid assumption when dealing with some tetraphenylborides in protic solvents (*vide infra*), especially water.

The assumptions have been expressed in terms of solvation of the silver cation, because solubility products, K^{M} (M denotes methanol) and K^{S}, of sparingly soluble silver salts, AgX, are easily measured potentiometrically.[17] Thus log $^{M}\gamma^{S}{}_{X^-}$ can be calculated from (1) if log $^{M}\gamma^{S}{}_{Ag^+}$ is known. Hence log $^{M}\gamma^{S}{}_{A^+}$ and log $^{M}\gamma^{S}{}_{B^-}$ can be found for all ions, if appropriate solubility or electrochemical measurements on electrolytes AX and AB[1,3,4] have been made.

$$\log\frac{K^{S}}{K^{M}}(\mathrm{AgX}) = \log {}^{M}\gamma^{S}{}_{Ag^+} + \log {}^{M}\gamma^{S}{}_{X^-} \qquad (1)$$

Another advantage of knowing log ${}^{M}\gamma^{S}{}_{Ag^+}$ is that liquid junction potentials[4,11,18] between methanol and solvent S can be evaluated from the observed EMF of cell A at 25°, as in eq 2. If liquid junction potentials (E_{LJ}) are known, then electrochemical methods can be used to obtain free energies of transfer of solutes,[3] provided that other half-cells in the same pair of solvents have comparable liquid junction potentials.

$$\begin{array}{l|l||l|l} \text{Ag} & \text{AgNO}_3 & \text{AgNO}_3 & \text{Ag} \qquad\qquad\qquad\qquad\qquad \text{(A)} \\ & 0.01\ M \text{ in} & 0.01\ M \text{ in} & \text{(Bridge saturated NEt}_4\text{ picrate in MeOH} \\ & \text{methanol} & \text{solvent S} & \text{or solvent S)} \end{array}$$

$$\Delta E = 0.0591 \log {}^{M}\gamma^{S}{}_{Ag^+} - E_{LJ} \qquad (2)$$

Solubilities, expressed as solvent activity coefficients relative to methanol,[1] are in Table I. The value of Ph_4AsBPh_4 in water has been estimated indirectly from eq 3. A very different value is obtained from (3) if

$$\log {}^{M}\gamma^{W}{}_{Ph_4AsBPh_4} = \log \frac{K^M}{K^W}(Ph_4AsX) - \log \frac{K^M}{K^W} \times$$

$$(KX \text{ or } CsX) + \log \frac{K^M}{K^W}(KBPh_4 \text{ or } CsBPh_4) \qquad (3)$$

$$(W = \text{water})$$

solubility products for silver salts, corresponding to the potassium or cesium salts in (3), are used.[1] The solubility products of $AgBPh_4$ in water and to a lesser extent in methanol, as measured potentiometrically, do not appear to obey the relationships expressed by (1) and (3).[1] This has been noted in the following calculations. The other solvent activity coefficients in Table I and part XII[1] are consistent when manipulated algebraically as in (3) to give solvent activity coefficients of other electrolytes. The assumptions are as follows.

Group 1. Log ${}^{M}\lambda^{S}{}_{A^+}$ = Log ${}^{M}\lambda^{S}{}_{B^-}$. This is applied to situations where A^+ and B^- are large symmetrical ions of similar size and structure. The charge is on an atom which is "buried" under the same ligands. Examples are the tetraphenylarsonium–tetraphenylboride (TATB) assumption[1,12,14] (eq 4 and 5) and the Popovych[5] assumption (eq 6), in which solubility products, K, are manipulated. The results are in Table VI

$$\log \frac{K^M}{K^S}(AgBPh_4) - {}^1\!/_2 \log \frac{K^M}{K^S}(Ph_4AsBPh_4) =$$

$$\log {}^{M}\gamma^{S}{}_{Ag^+} \qquad (4)$$

$$\log \frac{K^M}{K^S}(AgX) - \log \frac{K^M}{K^S}(Ph_4AsX) +$$

$${}^1\!/_2 \log \frac{K^M}{K^S}(Ph_4AsBPh_4) = \log {}^{M}\gamma^{S}{}_{Ag^+} \qquad (5)$$

$$\log \frac{K^M}{K^S}(AgCl) - \log \frac{K^M}{K^S}(KCl) + \log \frac{K^M}{K^S}(KBPh_4) -$$

$${}^1\!/_2 \log \frac{K^M}{K^S}(TAB\ BPh_4) = \log {}^{M}\gamma^{S}{}_{Ag^+} \qquad (6)$$

$$(TAB = \text{triisoamylbutylammonium})$$

as TATB assumptions 1 and 2. Very different results are obtained from (4) and (5), for water as solvent. As noted, this may be due to the unreliable value for $AgBPh_4$ in water. The value from TATB assumption 2 is preferred The TATB assumption 3 uses acetonitrile as reference solvent, rather than methanol. Values of log ${}^{CH_3CN}\gamma^{S}{}_{Ag^+}$ are calculated from data in Table I, using an equation corresponding to (4). This was done because of some uncertainty about our value for $AgBPh_4$ in methanol.[1] The values for log ${}^{M}\gamma^{S}{}_{Ag^+}$, recorded as TATB assumption 4, are calculated as in (7) on the assumption, which emerges from other data in Table VI, that log ${}^{M}\gamma^{CH_3CN}{}_{Ag^+}$ is −6.3. This latter assumption was remembered when evaluating the overall picture given by Table VI and recorded there as "our estimate."

$$\log \frac{K^{CH_3CN}}{K^S}(AgBPh_4) - {}^1\!/_2 \log \frac{K^{CH_3CN}}{K^S}(Ph_4AsBPh_4) -$$

$$6.3 = \log {}^{M}\gamma^{S}{}_{Ag^+} \qquad (7)$$

Group 2. Log ${}^{M}\gamma^{S}{}_{B^-}$ = Log ${}^{M}\gamma^{S}{}_{C}$. The solutes are chosen so that the large uncharged species, C, is thought to have the sum of all its interactions with the solvent the same as those of the large anion, B^-, except for the electrostatic interaction. For very large anions, the electrostatic interaction is assumed to be unchanged for transfer through solvent, especially those of comparable dielectric constant, as is the case here. The structures of B^- and C should be as similar as possible for this assumption to be valid.

The tetraphenylmethane–tetraphenylboride (TMTB) assumption[14] (8) is of this type, as are two which were implied in an earlier paper,[18] the iodine-triiodide assumption (eq 9 and 10) and the SNAr transition state reactant molecule assumptions[19] (eq 11 and 12). A related assumption by De Ligny and Alfenaar[22] is included in this group, where the asterisk assumes that

$$\log \frac{K^M}{K^S}(AgBPh_4) - \log \frac{S^M}{S^S}(Ph_4C) = \log {}^{M}\gamma^{S}{}_{Ag^+} \qquad (8)$$

$$\log \frac{K_i{}^M}{K_i{}^S}(I_3^-) = \log {}^{M}\gamma^{S}{}_{I_2} - \log {}^{M}\gamma^{S}{}_{I_3^-} +$$

$$\log {}^{M}\gamma^{S}{}_{I^-} = {}^*\!\log {}^{M}\gamma^{S}{}_{I^-} \qquad (9)$$

$$\log \frac{K^M}{K^S}(AgI) - \log \frac{K_i{}^M}{K_i{}^S}(I_3^-) = \log {}^{M}\gamma^{S}{}_{Ag^+} \qquad (10)$$

$$\log \frac{K^M}{K^S}(AgY) - \log \frac{k^S}{k^M}(ArX + Y^-) = \log {}^{M}\gamma^{S}{}_{Ag^+} \qquad (11)$$

$$\log \frac{k^S}{k^M} = \log {}^{M}\gamma^{S}{}_{ArX} - \log {}^{M}\gamma^{S}{}_{ArXY^{\ddagger}} +$$

$$\log {}^{M}\gamma^{S}{}_{Y^-} = {}^*\!\log {}^{M}\gamma^{S}{}_{Y^-} \qquad (12)$$

${}^{M}\gamma^{S}{}_{I_2} = {}^{M}\gamma^{S}{}_{I_3^-}$ or that ${}^{M}\gamma^{S}{}_{ArX} = {}^{M}\gamma^{S}{}_{ArXY^{\ddagger}}$. In eq 8–12, K's are solubility products (mole^2 l.$^{-2}$)[1,17] and S's are solubilities (mole l.$^{-1}$) from Table I, K_i's (mole l.$^{-1}$) are instability constants of triiodide[17,18] ion from Table II, and k's are rate constants (l. mole^{-1} sec^{-1}) for aromatic nucleophilic substitution reactions (13) of 4-nitrophenyl or 2,4-dinitrophenyl halides,[18,20] from

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(19) Many transition states, *e.g.*, of SN2 reactions of methyl chloride, do have specific interactions with solvents.[20,21] The SNAr transition state reactant molecule assumption (eq 11 and 12) and the SN transition state assumption (eq 15) are *not* applicable to *all* SN reactions. They give effectively the same log ${}^{M}\gamma^{S}{}_{Ag^+}$, however, if applied to all SNAr reactions of nitro-activated aryl halides, or to SN2 reactions of SCN^- or I^- with methyl or butyl iodide.

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Table II. Instability Constants of Triiodide Ion and Solubility Products of Silver Iodide at 25°.[a] The Iodine–Triiodide Assumption

Solute	MeOH Log K_i[a]	Solvent: MeOH	H_2O	$HCONH_2$	DMF	DMAC	CH_3CN	DMSO	CH_3NO_2	TMS	NMePy	80 DMSO-M
$\log K_i^M - \log K_i^S = \log {}^{M}\gamma^{S}_{I_2} + \log {}^{M}\gamma^{S}_{I^-} - \log {}^{M}\gamma^{S}_{I_3^-}$												
I_3^- [d]	−4.3	0.0	−1.45	−0.6	2.8[b]	3.1	2.5	1.3[b,c]	2.9[b]	3.2[b]	3.0[b]	1.3[b]
$\log K^M - \log K^S = \log {}^{M}\gamma^{S}_{Ag^+} + \log {}^{M}\gamma^{S}_{I^-}$												
AgI	−18.3	0.0	−2.3	−3.8	−2.5	−3.6	−4.1	−6.9	4.3	0.4	−3.8	−5.9
$\log K^M - \log K^S - \log K_i^M + \log K_i^S = \log {}^{M}\gamma^{S}_{Ag^+}$ [e]												
$\log {}^{M}\gamma^{S}_{Ag^+}$		0.0	−0.8 ±0.2	−3.2 ±0.4	−5.3 ±0.3	−6.7 ±0.3	−6.6 ±0.4	−8.2 ±0.4	1.4 ±0.4	−2.8 ±0.4	−6.8 ±0.4	−7.2 ±0.3

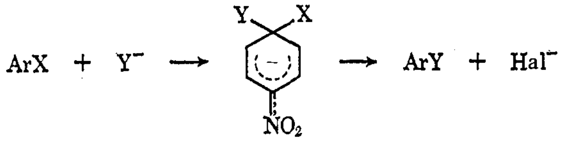
[a] Instability constants K_i are in mole l.$^{-1}$; solubility products, K, are in mole^2 l.$^{-2}$; data from ref 17 and Table I unless stated otherwise. [b] This work. [c] The instability constant of $10^{-6.9}$ mole l.$^{-1}$ for triiodide ion in DMSO given in ref 17 is incorrect. The value is $10^{-5.4}$. [d] The maximum limit of uncertainty is estimated as ±0.1 log unit for the difference between these instability constants. A complex curve was obtained for the potentiometric titration of iodine with iodide ion in hexamethylphosphoramide, and the instability constant was not calculated in HMPT. [e] On the assumption that ${}^{M}\gamma^{S}_{I_2} = {}^{M}\gamma^{S}_{I_3^-}$; *cf.* eq 10.

Table III. Rates of Aromatic Nucleophilic Substitution Reactions at 25°. The Molecule–SNAr Transition State Assumption

Reactants RX + Y^-	Log k^M	Solvent: $HCONH_2$	DMF	DMAC	CH_3CN	DMSO	CH_3NO_2	TMS	NMePy	HMPT
$\log k^S/k^M = \log {}^{M}\gamma^{S}_{Y^-} + \log {}^{M}\gamma^{S}_{RX} - \log {}^{M}\gamma^{S}_{\ddagger}$										
$4\text{-}NO_2C_6H_4F + N_3^-$	−7.2[c]	...	4.5[c]	5.0[c]	3.9[c]	3.9[c]	3.5[c]	4.5[a,e]	5.3[a]	7.3[a]
$4\text{-}NO_2C_6H_4I + N_3^-$	−9.5[c]	...	4.2[c]	...	3.8[a]	...	...	...	4.7[a]	6.3[a]
$2,4\text{-}(NO_2)_2C_6H_3I + SCN^-$	−5.4[b]	−0.3[a]	1.7[b]	2.1[a]	1.6[a]	1.2[a]	1.3[a]	1.7[a,f]	2.0[a]	...
$2,4\text{-}(NO_2)_2C_6H_3I + Cl^-$	−10.2[a]	...	6.5[a]	...	...	...	...	...	...	8.8[a]
$\log {}^{M}\gamma^{S}_{AgY} - \log k^S/k^M = \log {}^{M}\gamma^{S}_{Ag^+}$ [d]										
		−3.7 ±0.2	−4.6 ±0.4	−5.4 ±0.2	−5.4 ±0.2	−8.5 ±0.2	2.8 ±0.2	−1.1 ±0.2	−5.8 ±0.3	−9.5 ±0.5

[a] This work. [b] Reference 20. [c] J. Miller and A. J. Parker, *J. Am. Chem. Soc.*, **83**, 117 (1961). [d] The assumption is that ${}^{M}\gamma^{S}_{ArX} = {}^{M}\gamma^{S}_{\ddagger}$ as in eq 11 and 12. [e] Rate constant at 30° was $10^{-2.50}$ M^{-1} sec^{-1}. This value is at 30° using log $k^M = -7.0$. [f] Rate constant at 30° was $10^{-3.52}$ M^{-1} sec^{-1}. This value is at 30° using log $k^M = -5.2$.

Table III. The SNAr reactions have large transition states, $ArXY^{\ddagger}$, which closely resemble the high energy intermediate complex shown in (13). Thus the structure of the reactant, ArX, and this transition state are similar. The consequences of these assumptions are shown in Table VI.


(13)

Group 3. Modifications of the Born Equation for Alkali Metal Cations. The assumptions labeled by us as the Izmailov,[3,13] Pleskov[3,10] and Strehlow,[3] Coetzee and Campion,[8] and Feakins and Watson[6] assumptions have been adequately described in the literature. These authors give data which lead to log ${}^{M}\gamma^{S}_{X^-}$ and we have calculated log ${}^{M}\gamma^{S}_{Ag^+}$ from solubilities of AgX in Table I, through eq 1. Coetzee and Campion[8] do not give data for methanol so that this has required an additional assumption on our part, that log ${}^{M}\gamma^{H_2O}_{Ag^+}$ is −0.8, in line with other data in Table VI.

Group 4. Log ${}^{M}\gamma^{S}_{A^+}$ = Log ${}^{M}\gamma^{S}_{C}$. Here A^+ is a protonated Hammett indicator and C is the uncharged form of the indicator.[3,9] Thus A^+ and C are of similar size and structure. A^+ becomes a H-bond donor though, which is unfortunate. The assumption listed in Table VI as the Kolthoff–Strehlow assumption is based on thorough studies of the polarography of the ferrocene–ferricinium and the cobaltocene–cobalticene redox systems.[3,4,11] The method has been discussed at length by Strehlow,[3] Kolthoff,[4] and Iwamoto.[11] Kolthoff and Thomas[4] show how log ${}^{0}\gamma^{S}_{Ag^+}$ is calculated *via* this assumption; we use their method to calculate the values in Table VI.

Group 5. Log ${}^{M}\gamma^{S}_{A^{3+}}$ = Log ${}^{M}\gamma^{S}_{A^{2+}}$. Iwamoto[11] has evaluated liquid junction potentials *vs.* sce, using polarography on iron(II) and iron(III) phenanthroline complexes. Because of discrepancies with other data in Table VI, we have also calculated his data[23] for acetonitrile as reference solvent and then converted to methanol as reference solvent, on the assumption made before that log ${}^{M}\gamma^{CH_3CN}_{Ag^+}$ is −6.3. Both sets of values are shown in Table VI.

Group 6. Negligible Liquid Junction Potential in Cell A.[18] The emf of cell A gives 0.0591 log ${}^{M}\gamma^{S}_{Ag^+} - E_{LJ}$, after correction for imcomplete dissociation of silver nitrate. Values are in Table IV. The liquid junction potentials recorded in Table IV are given by (14), where log ${}^{S_1}\gamma^{S_2}_{Ag^+}$ is calculated from "our estimate" for log

$$E_{LJ} = 0.0591 \log {}^{S_1}\gamma^{S_2}_{Ag^+} - \Delta E \qquad (14)$$

${}^{M}\gamma^{S}_{Ag^+}$ at the foot of Table VI. These liquid junction potentials should be applicable to a number of cells having salt bridges of saturated tetraethylammonium picrate in the appropriate solvents S_1 or S_2, provided that the ions in the half-cell are not too small.

The first assumption (6a) is that, if the bridge is saturated tetraethylammonium picrate in methanol or the solvent S,[18] then E_{LJ} is negligible. Values of log ${}^{M}\gamma^{S}_{Ag^+}$ follow from (2). The values in Table VI by

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(23) D. C. Luehrs, R. T. Iwamoto, and J. Kleinberg, *Inorg. Chem.*, **5**, 201 (1966).

Table IV. Emf of the Cell Ag|AgNO$_3$ $\overset{-}{(0.01}$ *M*) in S$_1$||AgNO$_3$ $\overset{+}{(0.01}$ *M*) in S$_2$|Ag at 25°[a]

S$_1$	S$_2$	ΔE_{obsd}, mV	ΔE_{cor},[b] mV	Log ${}^{S_1}\gamma^{S_2}_{Ag^+}$[c]	E_{LJ},[d] mV
H$_2$O[f]	MeOH[f]	75 ± 10	90	+1.5 ± 0.2	−40
H$_2$O[f]	HCONH$_2$[f]	−75 ± 5	−75	−1.3 ± 0.1	−90
H$_2$O[f]	DMF[f]	−90 ± 10	−70	−1.3 ± 0.2	−180
H$_2$O[f]	DMAC[f]	−125 ± 15	−110	−1.9 ± 0.3	−230
H$_2$O[f]	DMSO[f]	−235 ± 10	−235	−4.0 ± 0.2	−200
H$_2$O[f]	CH$_3$CN[f]	−150 ± 10	−135	−2.3 ± 0.2	−190
MeOH	HCONH$_2$	−190 ± 10	−210	−3.6 ± 0.2	−5
MeOH	DMF	−204 ± 0	−190	−3.2 ± 0.0	−110
MeOH	DMAC	−245 ± 10	−245	−4.2 ± 0.2	−140
MeOH	HMPT	−425 ± 15	−425	−7.2 ± 0.3	−160
MeOH	DMSO	−370 ± 10	−390	−6.6 ± 0.2	−90
MeOH[e]	CH$_3$NO$_2$[e]	200 ± 15	200	+3.4 ± 0.3	−100
MeOH	TMS	55 ± 10	55	+1.0 ± 0.2	−180
MeOH	CH$_3$CN	255 ± 5	−255	−4.3 ± 0.1	−120
MeOH	80 DMSO-M	−300 ± 10	−310	−5.2 ± 0.2	−140
HCONH$_2$	CH$_3$CN	−45 ± 5	−30	−0.5 ± 0.1	−120
HCONH$_2$	DMF	35 ± 5	50	+0.8 ± 0.1	−130
HCONH$_2$	DMAC	−30 ± 10	−20	−0.3 ± 0.2	−150
HCONH$_2$	DMSO	−130 ± 10	−130	−2.3 ± 0.2	−130
CH$_3$CN	TMS	300 ± 10	310	+5.2 ± 0.2	−50
CH$_3$CN	DMF	40 ± 0	50	+0.8 ± 0	+20
CH$_3$CN	80 DMSO-M	−65 ± 10	−85	−1.5 ± 0.2	+20
CH$_3$CN	DMAC	−30 ± 5	−30	−0.5 ± 0.1	+10
CH$_2$CN	DMSO	−135 ± 5	−145	−2.5 ± 0.1	+30
CH$_3$CN[e]	CH$_3$NO$_2$[e]	465 ± 15	465	+7.9 ± 0.3	+5
CH$_3$CN	HMPT	−200 ± 30	−200	−3.4 ± 0.6	−20
DMF	DMAC	−60 ± 0	−70	−1.3 ± 0	−10
DMF	DMSO	−180 ± 10	−200	−3.4 ± 0.2	+20
DMF	HMPT	−235 ± 10	−235	−4.0 ± 0.2	−50
DMSO	DMA	120 ± 10	130	+2.3 ± 0.2	−40
DMSO	80 DMSO-M	50 ± 10	50	+0.8 ± 0.2	−5

[a] Bridge is saturated NEt$_4$Pic in S$_1$, in S$_2$, and in 50:50 S$_1$:S$_2$. The values shown were obtained within these limits using any one of these three bridge solvents and using AgClO$_4$ in place of AgNO$_3$. [b] An attempt has been made to allow for incomplete dissociation of 0.01 *M* AgNO$_3$ using the following degrees of dissociation. In MeOH $\alpha = 0.62$: R. S. Drago and K. F. Purcell, "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965; in DMF $\alpha = 0.42$: H. C. Chateau and M. C. Moncet, *Compt. Rend.*, **256**, 1504 (1963); and in CH$_3$CN $\alpha = 0.63$: ref 4. Silver nitrate is a strong electrolyte in water, formamide, and DMSO.[15] The following values are not known but are assumed from the values for related solvents, following values of log ${}^{M}\gamma^{S}_{Ag^+}$ in Table VI, the dielectric constant of the solvent, and the expected solvation of nitrate ion. In CH$_3$NO$_2$ $\alpha = 0.3$; in HMPT $\alpha = 0.6$; in TMS $\alpha = 0.3$; and in NMePy $\alpha = 0.6$. The emf's of the cells were within the uncertainty limits, when 10^{-3} *M* AgNO$_3$ in dipolar aprotic solvents was used in each half-cell, but tended toward ΔE_{cor}. [c] From eq 14, assuming no liquid junction potential. [d] From eq 14, assuming that log ${}^{S_1}\gamma^{S_2}_{Ag^+}$ is "our estimate" in Table VI. [e] 10^{-3} *M* AgClO$_4$ only. [f] 10^{-2} *M* AgNO$_3$ only.

Table V. Rates of SN2 Reactions[a] at 25°. The SN Transition State Assumption

Reactants RI + Y$^-$	MeOH Log k^M	Solvent MeOH	H$_2$O	HCONH$_2$	DMF	DMAC	CH$_3$CN	NMePy	CH$_3$NO$_2$	DMSO	HMPT	80 DMSO-M
		Log k^S/k^M = Log ${}^{M}\gamma^{S}_{Y^-}$ + Log ${}^{M}\gamma^{S}_{RI}$ − Log ${}^{M}\gamma^{S}_{\ddagger}$										
CH$_3$I + SCN$^-$	−3.3	0.0	−0.2	0.5	2.1	2.5	1.4	3.5	1.3	..	...	1.6
CH$_3$I + I$^-$	−2.5	0.0	−0.8	...	...	...	...	...	...	...	...	...
n-BuI + SCN$^-$	−4.5	0.0	...	...	1.9	...	...	...	...	1.7	3.3	...
4-NO$_2$C$_6$H$_4$I + N$_3^-$	−9.5	0.0	...	...	4.2	...	3.8	4.7	...	...	6.3	...
RI	Log S^M[b]	Log S^M − Log S^S = Log ${}^{M}\gamma^{S}_{RI}$										
4-NO$_2$C$_6$H$_4$I	−1.6	0.0	...	0.4	−1.2	...	−0.4	−1.4	−0.6	...	−1.5	−0.8
	Log *h*/*c* (M)[c]	Log *h*/*c*(S) − Log *h*/*c*(M) = Log ${}^{M}\gamma^{S}_{RI}$										
CH$_3$I	2.20	0.0	1.4	0.4	−0.6	−0.6	−0.4	−0.7	−0.2	−0.4	−0.7	−0.3
C-BuI	2.1	0.0	...	...	−0.3	...	−0.3	...	...	−0.0	−0.3	...
		Log ${}^{M}\gamma^{S}_{AgY}$ − Log k^S/k^M + Log ${}^{M}\gamma^{S}_{RI}$ = Log ${}^{M}\gamma^{S}_{Ag^+}$[d]										
		0.0	−0.2 ±0.4	−4.0 ±0.3	−5.1 ±0.4	−6.5 ±0.3	−5.8 ±0.3	−7.3 ±0.6	+2.6 ±0.3	−8.5 ±0.3	+10.3 ±0.3	−7.7 ±0.3

[a] Rate constants are from papers published in this series and from ref 21 (part XIV). [b] *S* is the solubility in mole l.$^{-1}$, measured by analyzing saturated solutions. [c] This is the Henry's law constant (mm l. mole^{-1}) in methanol, M, and solvent S. [d] This is the assumption that log ${}^{M}\gamma^{S}_{\ddagger}$ is zero: *cf.* eq 15.

this method are reasonable, in terms of other values in Table VI, for the three protic solvents. We therefore assume (6a) that *there is no liquid junction potential in cell A when S is water or formamide and the reference solvent is methanol.*

Because the values from 6a are anomalous for dipolar aprotic solvents, in terms of other values in Table VI, we examine another assumption, 6b, that there is no liquid junction potential in cell A, when methanol is replaced by acetonitrile as reference solvent and S is also

Table VI. Extrathermodynamic Assumptions Leading to Log ${}^{M}\gamma^{S}_{Ag^+}$ at 25° [a]

		Solvent										
Assumptions	Uncertainty	H_2O	$HCONH_2$	DMF	DMAC	DMSO	CH_3CN	HMPT	CH_3NO_2	TMS[b]	NMePy	80 DMSO-M
Group 1. ${}^{M}\gamma^{S}_{A^+} = {}^{M}\gamma^{S}_{B^-}$												
(a) TATB assumptions[c]		−6.9	−3.6	−4.6	−5.4	−6.6	−5.1	−6.5	...	−2.4	...	...
1. $AgBPh_4 - {}^1\!/_2 Ph_4AsBPh_4$[d]	±0.4											
2. $AgX - Ph_4AsX - {}^1\!/_2 Ph_4AsBPh_4$[e]	±0.6	−1.3	−3.9	−4.8	...	...	−6.3	...	...	...	...	...
3. $AgBPh_4 - {}^1\!/_2 Ph_4AsBPh_4$[f]	±0.2	...	...	+0.5[f]	−0.3[f]	−1.5[f]	0.0[f]	−1.5[f]	...	+2.7[f]	...	...
4. ${}^{M}\gamma^{CH_3CN}_{Ag^+} = -6.3$[g]	±0.2	...	...	−5.8	−6.6	−7.8	(−6.3)[g]	−7.8	...	−3.6	...	...
(b) Popovych[h]		−1.0	...	...	...	...	...	...	...	...	...	...
Group 2. ${}^{M}\gamma^{S}_{B^-} = {}^{M}\gamma^{S}_{C}$												
$AgBPh_4$–Ph_4C (TMTB)[c,i]	±0.5	...	...	−5.6	−6.6	...	−6.2	...	...	...	...	...
Triiodide–iodine[j]	±0.4	−0.8	−3.2	−5.3	−6.7	−8.2	−6.6	...	+1.4	−2.8	−6.8	−7.2
Molecule–SNAr TS[k]	±0.3	...	−3.7	−4.6	−5.4	−8.5	−5.4	−9.5	+2.8	−1.1	−5.8	...
De Ligny–Alfenaar[l]	±1	−0.5	...	...	...	...	...	...	...	...	...	...
Group 3. Born												
Feakins–Watson[m]	...	+2.7	...	...	...	...	...	...	...	...	...	...
Izmailov[n]	...	−2.1	...	...	...	...	−6.3	...	...	...	...	...
Coetzee–Campion[o]	...	*x*[o]	...	...	...	...	$-2.8 + x$					
Pleskov–Strehlow[p]	...	−0.4	−1.9	...	...	...	−6.9	...	...	...	...	...
Coetzee–Campion[o,q]	...	(−0.8)[q]	...	...	...	...	−3.6	...	...	...	...	...
Group 4. ${}^{M}\gamma^{S}_{A^+} = {}^{M}\gamma^{S}_{C}$												
Hammett H_0[p]	...	+0.3	−1.8	...	...	...	−5.3	...	...	...	...	...
Kolthoff–Strehlow[p]	...	+0.8	−2.7	...	...	...	−6.1	...	...	...	...	...
Group 5. ${}^{M}\gamma^{S}_{A^{3+}} = {}^{M}\gamma^{S}_{A^{2+}}$												
Iwamoto[r]	...	+3.8	...	...	...	−5.2	−3.6	...	...	...	...	...
Iwamoto[r]–${}^{M}\gamma^{A}_{Ag^+} = -6.3$[s]	...	+1.1[g,s]	...	...	...	−7.9[g,s]	(−6.3)[s]	...	...	...	...	...
Group 6. No E_{LJ}												
6a ref: MeOH[t]	±0.2	−1.5	−3.6	−3.2	−4.2	−6.6	−4.3	−7.2	+3.4	+1.0	...	−5.2
6b ref: CH_3CN[u]	±0.3	+2.3[u]	+0.5[u]	+0.8	−0.5[u]	−2.5[u]	0.0[u]	−3.4[u,x]	+7.9[u]	+5.2[u]	...	−1.5[u]
6c log ${}^{M}\gamma^{CH_3CN} =_{Ag^+} -6.3$[v]	±0.3	...	...	−5.5	−6.8	−8.8	(−6.3)[v]	−9.7	+1.6	−1.1	...	−7.8
Group 7. ${}^{M}\gamma^{S}_{SN\ddagger} = 1$[w]	±0.3	−0.2	−4.0	−5.1	−6.5	−8.5	−5.8	−10.3	+2.6	...	−7.3	−7.7
Our estimate		−0.8	−3.7	−5.1	−6.6	−8.2	−6.3	−10	+1.7	−2	−6.8	−7.4

[a] Reference solvent methanol unless stated otherwise. Molar concentration scale. [b] Data for tetramethylene sulfone were measured at 30°. [c] Solubility data from Table I. [d] Calculated from eq 4. [e] Equation 5. X is picrate or iodide; *cf.* ref. 1. [f] Reference solvent is acetonitrile; these are values of log ${}^{CH_3CN}\gamma^{S}_{Ag^+}$ calculated from eq 4 with acetonitrile rather than methanol as reference solvent. [g] The additional assumption is made that log ${}^{M}\gamma^{CH_3CN}_{Ag^+}$ is −6.3, based on other data in this table. These values of log ${}^{M}\gamma^{S}_{Ag^+}$ are calculated from log ${}^{M}\gamma^{S}_{Ag^+}$ = log ${}^{CH_3CN}\gamma^{S}_{Ag^+} - 6.3$. [h] Reference 5. [i] Equation 8. [j] Data from Table II, values calculated from eq 10. [k] Data from Table III, calculated from eq 11. [l] Calculated from values of log ${}^{M}\gamma^{H_2O}_{Br^-}$ and log ${}^{M}\gamma^{W}_{Cl^-}$ in ref 22 using AgX solubility data from Table I in eq 1. [m] Using log ${}^{M}\gamma^{H_2O}_{Cl^-} = -5.8$ from ref 6, and AgCl solubility data from Table I in eq 1. [n] Values of ${}^{M}\gamma^{S}_{X^-}$ from ref 3, Table XVI, Chapter 4. The quoted value is calculated from AgX solubility data in Table I through eq 1. [o] Using values of ${}^{H_2O}\gamma^{CH_3CN}_{X^-}$ from ref 8 and AgX solubility data from Table I in eq 1 with water as reference solvent, and denoting the unknown value of log ${}^{M}\gamma^{H_2O}_{Ag^+}$ by *x*. [p] Using ${}^{M}\gamma^{S}_{H^+}$ or ${}^{M}\gamma^{S}_{Rb^+}$ from ref 3, Tables XIII, XIV, or XV, Chapter 4, with standard electrode potentials for silver in ref 3, Table II, Chapter 4. Where this is not available by using solubilities of cesium and rubidium salts from ref 3 and 17 and standard electrode potentials of rubidium (ref 3) on the assumption that ${}^{M}\gamma^{S}_{Rb^+} \approx {}^{M}\gamma^{S}_{Cs^+}$, to calculate ${}^{M}\gamma^{S}_{Hal^-}$ and hence ${}^{M}\gamma^{S}_{Ag^+}$ from solubilities of AgX in Table I through eq 1. [q] The additional assumption is made that log ${}^{M}\gamma^{H_2O}_{Ag^+}$ (*x* above) is −0.8, based on other data in this table. [r] Reference 23. We assume that this assumption (ref 11) was used, but this is not clear from ref 23. [s] Values from ref 23, with acetonitrile as reference solvent, adjusted on the assumption that log ${}^{M}\gamma^{CH_3CN}_{Ag^+}$ is −6.3. [t] Data from Table IV. [u] Reference solvent is acetonitrile, data from Table IV. [v] Reference solvent methanol, calculated from (6b), on the assumption made in footnote *g* that log ${}^{M}\gamma^{CH_3CN}_{Ag^+} = -6.3$; *i.e.*, log ${}^{M}\gamma^{S}_{Ag^+}$ = log ${}^{CH_3CN}\gamma^{S}_{Ag^+} - 6.3$. We assume that there is no liquid junction potential between dipolar aprotic solvents. [w] Data from Table V. [x] Uncertainty is ±0.6.

a dipolar aprotic solvent; *i.e.*, assumption 6b is that *there is no liquid junction potential when both solvents are dipolar aprotic in cell A*. The values obtained from 6b relative to acetonitrile are converted to methanol as reference solvent by assuming, as before, that log ${}^{\mathrm{M}}\gamma^{\mathrm{CH_3CN}}{}_{\mathrm{Ag^+}}$ is -6.3. The division into protic and dipolar aprotic solvents is not a sharp one, however (*cf.* N-methylformamide[15]), so that assumptions 6a and 6b have unsatisfactory features.

Group 7. The SN Transition State Assumption ${}^{\mathrm{M}}\gamma_{\ddagger}{}^{\mathrm{S}} = 1$. This assumption is applied to large SN2 or SNAr transition state anions, which do not have specific interactions, such as H bonding, with either solvent.[19] Reactions of methyl iodide or 4-iodonitrobenzene with large anions, such as thiocyanate or iodide ion, are well suited to this assumption. Values of log ${}^{\mathrm{M}}\gamma^{\mathrm{S}}{}_{\mathrm{Ag^+}}$ are calculated from (15), as in Table V.

$$\log \frac{K^{\mathrm{M}}}{K^{\mathrm{S}}}(\mathrm{AgY}) - \log \frac{k^{\mathrm{S}}}{k^{\mathrm{M}}}(\mathrm{RI} + \mathrm{Y^-}) + \log \frac{H^{\mathrm{S}}}{H^{\mathrm{M}}}(\mathrm{RI}) = \log {}^{\mathrm{M}}\gamma^{\mathrm{S}}{}_{\mathrm{Ag^+}} \quad (15)$$

In (15) the rate constants give log ${}^{\mathrm{M}}\gamma^{\mathrm{S}}{}_{\mathrm{Y^-}}$ + log ${}^{\mathrm{M}}\gamma^{\mathrm{S}}{}_{\mathrm{RI}}$ − log ${}^{\mathrm{M}}\gamma^{\mathrm{S}}{}_{\ddagger}$. The Henry's law constants[24] H^{S} and H^{M} (mm l. mole^{-1}) give log ${}^{\mathrm{M}}\gamma^{\mathrm{S}}{}_{\mathrm{R1}}$, so that if log ${}^{\mathrm{M}}\gamma^{\mathrm{S}}{}_{\ddagger}$ is assumed zero, log ${}^{\mathrm{M}}\gamma^{\mathrm{S}}{}_{\mathrm{Ag^+}}$ follows from (15). In one sense, this assumption is like those in group 3, based on the Born equation. A very large anion with well-dispersed charge is assumed to be similarly solvated by solvents of comparable bulk dielectric constant. Note that group 2 and group 7 cannot both be correct.

General Comments.

Our intuitive estimates of log ${}^{\mathrm{M}}\gamma^{\mathrm{S}}{}_{\mathrm{Ag^+}}$, after a not unbiased evaluation of the remarkable correspondence of values shown, are recorded in Table VI. Of all the assumptions, the triiodide–iodine (eq 9 and 10) is the easiest to use. It gives values close to our estimates and which are roughly the same as the TATB, the TMT*B*, the E_{LJ} (6a and 6c), the Popovych, and the SN transition state assumption. It is recommended for measurements on new solvents to those who can accept any assumptions in groups 1, 2, 6, or 7. It is realized[15] that iodine has strong specific interactions with those solvents in Table VI which are strong Lewis bases. Perhaps $\mathrm{I_3^-}$ is of comparable strength to iodine as a Lewis acid, or perhaps differences in size compensate for differences in acidity.

Although agreement is excellent for a large number of assumptions involving transfer of silver cation from methanol to acetonitrile, it seems likely that, when more data become available, group 3 will show greater divergence, if applied to solvents such as DMF and DMSO.

All the assumptions focus attention in one way or another on rather large, symmetrical solutes. With the exception of water and formamide, all the solvents have similar bulk dielectric constants (30–45).[12] This is a solvent situation where the simplest application of the Born equation would predict that electrostatic solvation be similar. Some of the agreement which we observe may not extend over a more representative group of solvents. It is difficult to study solvents of dielectric constants <30, because appropriate ion association constants are rarely known and ion association must be allowed for in such solvents.

The all important link between water and dipolar aprotic solvents is to us still uncertain, in view of the tetraphenylboride anomaly, the high dielectric constant of water, and its unusual structure. Further work on this aspect is needed.

Experimental Section

The purification of materials has been described previously[16–18] or was by standard procedures of distillation or recrystallization. Solubilities were determined potentiometrically for silver salts[17] and by analysis of saturated solutions, using our usual procedures,[1,17] for other salts. Instability constants were determined potentiometrically.[17] Rate constants were measured in the usual way.[18,20] Henry's law constants were obtained exactly as described by Grunwald and Winstein.[24] The emf of cell A was measured on a Radiometer pH meter, Type pHM 22 r.[17,18] Essentially the same emf was obtained with 0.01 *M* $\mathrm{AgClO_4}$ and 0.01 *M* $\mathrm{AgNO_3}$ in each half-cell. No special concessions were made to the fact that the solvents were dipolar aprotic except that they were used freshly distilled after drying with molecular sieves. All our experiments follow routine procedures, of physical chemistry, which are well established for aqueous solutions.

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