

Correlation of Solvent Effects on Rates of Solvolysis and S_N2 Reactions

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The effect of solvent transfer on rates of some classical S_N1 solvolyses and S_N2 reactions depends on the anion solvating properties of the solvents, as measured either by $\Delta G_{tr}(Cl^-)$ or by the changes in solvent acceptor number [$\Delta(AN)$]. For transfer through high dielectric ($\epsilon > 20$) solvents other than water, the transfer free energies of activation show the approximate linear free-energy relationships, $\Delta G_{tr}^\ddagger = n\Delta G_{tr}(Cl^-) = -n'\Delta(AN)$. These very simple relationships are extreme cases of the more precise expressions, $\Delta G_{tr}^\ddagger(S_{N1}) = p\Delta G_{tr}(K^+) + n\Delta G_{tr}(Cl^-) - \Delta G_{tr}(RX) = -p'\Delta(DN) - n'\Delta(AN) - \Delta G_{tr}(RX)$ and $\Delta G_{tr}^\ddagger(S_{N2}) = -n\Delta G_{tr}(Cl^-) - \Delta G_{tr}(RX) = n'\Delta(AN) - \Delta G_{tr}(RX)$. These expressions apply to a greater range of reactions and correlate rates in water and formamide as well as other less structured solvents. Even for "limiting" solvolyses of *tert*-butyl chloride and *p*-methoxyneophyl tosylate, cation solvation plays a significant role in S_N1 but not S_N2 reactions, if transfer is through a sufficiently wide range of low dielectric as well as high dielectric solvents. The usefulness of donor and acceptor numbers, as well as free energies of transfer of K⁺ and Cl⁻ as measures of cation and anion solvating power of solvents, is demonstrated.

Chemists have been seeking a simple method for predicting rates of reactions in different solvents.¹⁻⁹ This paper develops the linear free-energy relationships (eq 1 and 2) which, for several reactions in most polar solvents, reduce to the approximate relationships (eq 3). Equation 3 is a relationship of remarkable simplicity and although approximate, predicts several solvent effects on rate in a way that may be acceptable to many chemists.

$$\Delta G_{tr}^\ddagger(S_{N1}) = p\Delta G_{tr}(K^+) + n\Delta G_{tr}(Cl^-) - \Delta G_{tr}(RX) = -p'\Delta(DN) - n'\Delta(AN) - \Delta G_{tr}(RX) \quad (1)$$

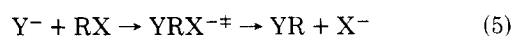
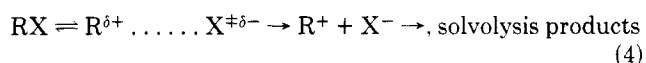
$$\Delta G_{tr}^\ddagger(S_{N2}) = -n\Delta G_{tr}(Cl^-) - \Delta G_{tr}(RX) \quad (2a)$$

$$= n'\Delta(AN) - \Delta G_{tr}(RX) \quad (2b)$$

$$\Delta G_{tr}^\ddagger(S_{N1} \text{ or } S_{N2}) = \pm n\Delta G_{tr}(Cl^-) = \mp n'\Delta(AN) \quad (3)$$

In eq 1, $\Delta G_{tr}^\ddagger(S_{N1})$ is the transfer free energy of activation for solvolysis reactions (eq 4) of carbon compounds, RX, and $\Delta G_{tr}^\ddagger(S_{N2})$ in eq 2 is the transfer free energy of activation for S_N2 reactions of anions Y⁻ with carbon compounds RX (eq 5). Transfer is from any polar reference solvent, o, to other solvents, s, and the effect (k^s/k^o) of solvent transfer on the rates, k , are related to ΔG_{tr}^\ddagger through eq 6. $\Delta G_{tr}(K^+)$ and $\Delta G_{tr}(Cl^-)$ in eq 1 and 2 are single ion free energies of transfer from the reference solvent to other solvents. They are based on the TATB assumption that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$.^{10,11} Values of $\Delta G_{tr}(RX)$ are experimentally determined free energies of solvent transfer for carbon com-

pounds, RX. The donor numbers (DN) and acceptor numbers (AN) are empirical parameters reflecting the donor and acceptor properties of the solvents¹² and p , n , p' , and n' are sensitivity parameters. The symbolism RX[‡] and YRX^{-‡} denotes the S_N1 and S_N2 transition states, respectively.



$$\Delta G_{tr}^\ddagger = -RT \ln (k^s/k^o) \quad (6)$$

Apart from the $\Delta G_{tr}(RX)$ term, eq 1 in part corresponds to the general forms of the multiparameter approaches proposed by Fawcett-Krygowski¹³ and Mayer¹⁴ in terms of the donor-acceptor description of solvent effects on equilibrium constants and rates of reaction. In the case of S_N2 reactions at carbon (eq 5) our expression (eq 2) differs from that proposed by Fawcett-Krygowski.¹³ Because cations and cationic centers are not involved in such S_N2 reactions we do not agree that solvent donor properties, e.g., cation solvating power, are a factor in determining rates of these reactions.

The transfer free energy of activation is given by eq 7 for S_N1 and by eq 8 for S_N2 reactions.²

$$\Delta G_{tr}^\ddagger(S_{N1}) = \Delta G_{tr}(RX^\ddagger) - \Delta G_{tr}(RX) \quad (7)$$

$$\Delta G_{tr}^\ddagger(S_{N2}) = \Delta G_{tr}(YRX^{-\ddagger}) - \Delta G_{tr}(RX) - \Delta G_{tr}(Y^-) \quad (8)$$

As several chemists have appreciated,¹⁻⁷ these equations allow interpretations of mechanism, but since ΔG_{tr} of transition states cannot be measured independently of a rate constant,

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they are only of limited value in predicting solvent effects on rate. One approach is to use ΔG_{tr} (model) for a real model solute as an indicator of $\Delta G_{tr}(RX^\ddagger)$ or $\Delta G_{tr}(YRX^{-\ddagger})$. The work of Abraham^{3,4} has been notable in this area and some preliminary developments¹ have been reviewed.²

Another approach is to estimate $\Delta G_{tr}(RX^\ddagger)$ and $\Delta G_{tr}(YRX^{-\ddagger})$ from the general anion and cation solvating properties of the solvents combined with estimates of the sensitivity of these "solutes" to such properties.¹⁵ This recognizes that $YRX^{-\ddagger}$ is an anion and that RX^\ddagger is a highly polar species, with well-developed cationic and anionic centers which will respond to the cation and anion solvating power of the solvents. Anion and cation solvating power is measured directly by $\Delta G_{tr}(Cl^-)$ (TATB) and $\Delta G_{tr}(K^+)$ (TATB), respectively. $\Delta G_{tr}(Cl^-)$ is very appropriate for S_N2 reactions; however, the donor-acceptor approach^{12,16} to molecular interactions has some advantages as a measure of ion solvating power in estimating $\Delta G_{tr}(RX^\ddagger)$ because RX^\ddagger is not an ion, but a highly polar "molecule" and there may be some conceptual difficulties in relating $\Delta G_{tr}(K^+)$ or $\Delta G_{tr}(Cl^-)$ for fully solvated ions to solvation of parts of the RX^\ddagger dipole.

Acceptor numbers are derived from the NMR chemical shifts of phosphorus which are produced on transfer of Et_3PO through solvents.¹² They are directly observable quantities and prove to be an excellent quantitative empirical solvent parameter for correlating those chemical phenomena which change with the electrophilic or acceptor properties of solvents.^{12,16} In the broadest possible sense of the word, acceptor numbers measure the ability of the solvents to "accept" (interact with) electron pairs from suitable donors in a variety of chemical situations.

Donor numbers measure the ability of solvents to donate electron pairs to suitable acceptors¹⁶⁻¹⁹ and have been defined as the negative of the enthalpy of adduct formation between the reference acid $SbCl_5$ and a solvent molecule in highly dilute 1,2-dichloroethane solution.

Despite occasional conceptual difficulties, especially relating to entropic effects,⁸ it is an indisputable fact that a remarkable amount of chemical information on systems in solution, be it a ΔG , ΔH , or other property, is correlated by the donor and acceptor numbers of solvents.¹⁶ The precise nature of the acceptor-donor interaction need not be specified. It could be H bonding, formation of an acid-base adduct, an ion-dipole interaction, covalent bonding, ion-ligand coordination, nucleophilic assistance, or electrophilic solvation of a leaving group. The advantage of the donor-acceptor correlations is that they bring many types of anion-molecule, cation-molecule, ion pair-molecule, and molecule-molecule interaction under one umbrella.

The advantage of such a general concept for estimating $\Delta G_{tr}(RX^\ddagger)$ is obvious. The S_N1 transition state RX^\ddagger for solvolysis of RX is indisputably highly dipolar,^{3,15} but it is not an ion pair, it is certainly not solvent separated ions, and it is very unlike "normal" polar organic molecules RX . Many chemists do not wish to be drawn into disputes about the type of interaction between solvent and RX in the transition state, but they are very interested in finding the most suitable solvent for a desired reaction. The concept of a donor interaction at $R^{\delta+}$ and an acceptor interaction at $X^{\delta-}$ between $R^{\delta+}\cdots X^{\delta-}$ and solvent does not require definition of the exact nature of RX^\ddagger , nor does it require a statement as to the precise nature of the interactions.¹⁶

There are limitations of course. The donor-acceptor correlations break down completely when interactions between soft acceptors (e.g., Cu^+ , Tl^+ , Zn^{2+}) and soft donors (e.g., N,N -dimethylthioformamide) take place. Back-bonding is not modeled by interactions of donors with $SbCl_5$. Acceptor numbers only have validity if they reflect chemical shifts for $Et_3PO\cdots A$ adduct formation, rather than (as with CF_3CO_2H)

protonation of triethylphosphine oxide.¹² Solvents which are weaker donors than dichloroethane (heptane) do not of course have meaningful donor numbers, other than to say they are less than zero.

Phenomenological Observations. With the background given above, we will first demonstrate some phenomenological relationships (eq 3) between the transfer free energy of activation of S_N1 and S_N2 reactions, anion solvating power, and solvent acceptor properties. We will then use eq 7 and 8 to see why these relationships develop and why, in some cases, deviations from the linear relationships (eq 3) occur.

Equations 9-12 summarize four relationships between transfer free energies of anions (Y^-)^{11,20,21} and cations (M^+)^{11,20-23} in high dielectric solvents, excluding soft cations in soft solvents, excluding other situations (e.g., Ag^+ in CH_3CN) where back-bonding is possible and excluding hydrophobic anions or cations (e.g., BPh_4^- , NBu_4^+) in water, where solvation is of the second kind. Some ΔG_{tr} (ion) values are in Tables I and II, but ref 11 and 20 contain additional values which fit eq 9-12.

Equation 9 summarizes the excellent correlation between solvation of potassium cation and solvation of other cations, including soft cations in hard solvents and hard cations in soft solvents.^{24,25} As shown in Table III, values of p decrease with decreasing surface charge of the cation ($Zn^{2+} > Cd^{2+} > Ba^{2+} > Li^+ > Na^+ > K^+ > Cs^+ > Ph_4As^+$). Thus $-\Delta G_{tr}(K^+)$ as recorded in Table II is a good measure of cation solvating power of solvents.²⁵ The more positive $-\Delta G_{tr}(K^+)$, the stronger the cation solvating power.

$$\Delta G_{tr}(M^+) = p \Delta G_{tr}(K^+) \quad (9)$$

$$\Delta G_{tr}(Y^-) = n \Delta G_{tr}(Cl^-) \quad (10)$$

$$\Delta G_{tr}(M^+) = -p' \Delta(DN) \quad (11)$$

$$\Delta G_{tr}(Y^-) = -n' \Delta(AN) \quad (12)$$

Data in Table I and II in ref 11 and 20 show that anion solvating power is effectively measured by $-\Delta G_{tr}(Cl^-)$ as in eq 10, with sensitivity (n) decreasing with decreasing anionic surface charge ($OAc^- > Cl^- > Br^- > I^- > ClO_4^-$; Table III).

Potassium ion solvating power (and thus general cation solvating power through eq 9) is well measured by solvent donor properties (eq 11), as shown in Figure 1 and Table II. Chloride ion solvating power (and thus general anion solvating power through eq 10) is well measured by solvent acceptor properties (eq 12), as shown in Figure 2 and Table II.

Equations 9-12 are of great value in correlating many aspects of solution chemistry, but in this paper we are concerned only with kinetics of S_N1 and S_N2 reactions. The expressions $-\Delta G_{tr}(K^+)$ or $+1.30 \Delta(DN)$ are equivalent as measures of the cation solvating power of solvents. Values of $-\Delta G_{tr}(Cl^-)$ or $+1.30 \Delta(AN)$ are equivalent as measures of anion solvating power, as shown in Table II. We expect that eq 11 or 12 will only give lower limits to $\Delta G_{tr}(M^+)$ or $\Delta G_{tr}(Y^-)$ when transfer is to solvents of very low dielectric constant (<5) like dioxane and ether. This is because Born type solvation is the major contributor to $\Delta G_{tr}(\text{ion})$ for such extreme transfers and this is not well measured by donor and acceptor numbers.

S_N2 Reactions. Transfer free energies of activation for many S_N2 reactions like eq 5 have simple linear free-energy relationships (eq 13-15) with $\Delta G_{tr}(Y^-)$, $\Delta G_{tr}(Cl^-)$, and $\Delta(AN)$ as shown in Table IV. Values of n'' , n , and n' are in Table III and express the sensitivity of each reaction to solvent transfer.

$$\Delta G_{tr}^\ddagger(S_N2) = -n'' \Delta G_{tr}(Y^-) \quad (13)$$

$$\Delta G_{tr}^\ddagger(S_N2) = -n \Delta G_{tr}(Cl^-) \quad (14)$$

Table I. Free Energies of Transfer of Ions from DMF at 25 °C (kJ g-ion⁻¹).
TATB Assumption $\Delta G_{tr}(\text{Ph}_4\text{As}^+) = \Delta G_{tr}(\text{Ph}_4\text{B}^-)$

Solvent ^a	ΔG_{tr}^b (Br ⁻)	ΔG_{tr}^b (N ₃ ⁻)	ΔG_{tr}^b (I ⁻)	ΔG_{tr}^b (SCN ⁻)	ΔG_{tr} (NMe ₄ ⁺) ^{d,f}	ΔG_{tr} (Me ₃ S ⁺) ^{e,f}	ΔG_{tr}^b (Ag ⁺)
CF ₃ CH ₂ OH	-41		-25				66
H ₂ O	-34	-35	-18	-16	5		17
HCONH ₂	-24	-23	-11	-12			2
MeOH	-23	-24	-10	-10	11	13	24
NMeF	-19						2 ^g
EtOH	-15	-18	-4		15	16	20 ⁱ
Me ₂ SO	-7	-11	-9 ^c	-8 ^c	3		-17
MeNO ₂		-10	-6	-7	6	11	43
PC		-6	-6	-7			33
MeCN	-3	-6	-4	-3	8	11	-5
DMF	0	0	0	0	0	0	0
DMA		-1	-2	1		1	-5
NMePy	1	6	0	3	2		-7 ⁱ
Me ₂ CO	8	9	8		8	12	25 ⁱ
HMPT		13	12	6			-26 ⁱ
0.70 Me ₂ SO-H ₂ O			-9 ^j	-8 ^j			
0.32 Me ₂ SO-H ₂ O		-17 ^j	-10 ^j	-8 ^j			

^a Abbreviations as in Table II. ^b From $\Delta G_{tr}(\text{AgX})^{11,20} - \Delta G_{tr}(\text{Ag}^+)$ (TATB), this table. ^c Dubious value because of high solubility of AgX and complex formation. ^d From $\Delta G_{tr}(\text{Me}_4\text{NI})^3 - \Delta G_{tr}(\text{I}^-)$, this table. ^e From $\Delta G_{tr}(\text{Me}_3\text{S}^+) - \Delta G_{tr}(\text{Ag}^+)^2 + \Delta G_{tr}(\text{Ag}^+)$ (TATB), this table. ^f Values are somewhat uncertain because of the high solubility of Me₄NI and Me₃SX in many solvents and the possibility of solvates. This is why we prefer $\Delta G_{tr}(\text{K}^+)$ as a measure of cation solvating power. ^g H. Schneider and C. Kalidas, private communication based on the ferrocene assumption, cf. ref 10 and 20. ^h Reference 11. ⁱ Reference 22. ^j Reference 2.

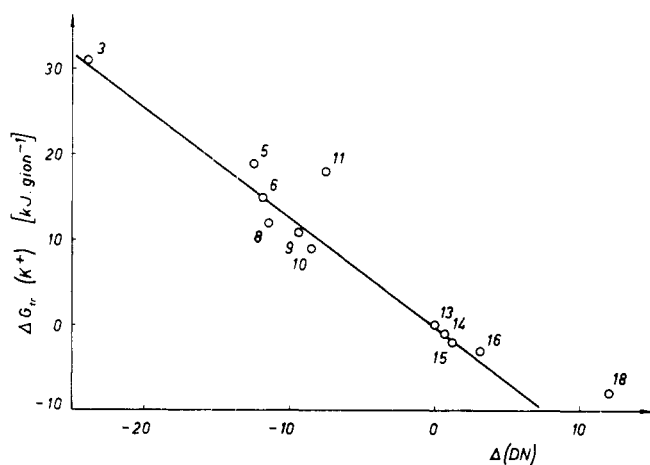


Figure 1. Relationship between potassium cation solvating power and solvent donor properties. Plot of the equation $\Delta G_{tr}(\text{K}^+) = -1.30\Delta(\text{DN})$ of eq 9 and 11 and Table II. Solvent data points are numbered as in Table II.

$$\Delta G_{tr}^\ddagger(\text{S}_\text{N}2) = n'\Delta(\text{AN}) \quad (15)$$

Transfer is through any set of polar solvents of high dielectric constant (>10), provided that the observed rate constants are for reaction of free anions Y⁻, rather than ion pairs.

As shown in Tables III and IV, the relationship is even simpler for some S_N2 reactions of iodomethane and for most S_NAr reactions in that n'' in eq 13 is unity. Equations 14 and 15 follow as corollaries of eq 13, through eq 10 and eq 12, respectively. Thus n in eq 14 is n'' (eq 13) × n (eq 10) and n' (eq 15) is n'' (eq 13) × n' (eq 12). This is confirmed in Table III.

The attempted correlations for water and formamide are instructive. As shown in Table IV, water and formamide are quite well correlated by eq 13–15 for reaction 6 of 4-fluoronitrobenzene with azide ion, reaction 5 of 2,4-dinitroiodobenzene with SCN⁻, and reaction 3 of iodomethane with SCN⁻, where n'' is unity. However, for all other reactions in Table IV, S_N2 reactions in water and formamide are up to 15 kJ

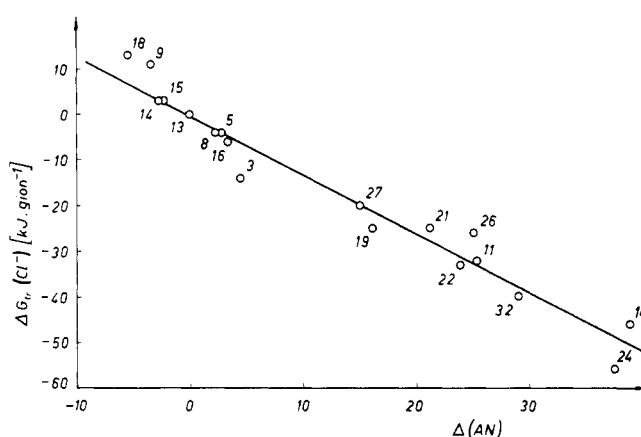


Figure 2. Relationship between chloride anion solvating power and solvent acceptor properties. Plot of the equation $\Delta G_{tr}(\text{Cl}^-) = -1.30\Delta(\text{AN})$ of eq 12 and 10 and Table II. Solvent data points are numbered as in Table II.

mol⁻¹ faster in terms of $\Delta G_{tr}^\ddagger(\text{S}_\text{N}2)$ than required by eq 13–15. This is true, even for reactions where n'' is unity, e.g., CH₃I + Cl⁻ (reaction 1).

We note from Table III that values of n'' in eq 13 of less than unity are observed if the transition state is loose;²⁶ e.g., for displacement at the methyl of the tosylate by azide ion, n'' is only 0.5, for reaction 4 of n-butyl bromide with azide ion, n'' is 0.73, and for reaction of bromomethane with Cl⁻, n'' is 0.80. Values of n'' from eq 13 can give valuable mechanistic information as to the tight or loose nature of S_N2 transition states.^{2,26}

The choice of eq 13, 14, or 15 for predicting rates of S_N2 reactions, or deriving values of n, n', or n'' to provide mechanistic information as to tightness or looseness, etc., of transition states, will depend on which parameters, $\Delta G_{tr}(Y^-)$, $\Delta G_{tr}(\text{Cl}^-)$, or $\Delta(\text{AN})$, are available. Equation 13 has the most direct mechanistic significance, as we will see, but the parameters for eq 14 and 15 are more precise and more are available. Equation 13 of course provides a way of measuring $\Delta G_{tr}(Y^-)$, eq 14 a way of measuring $\Delta G_{tr}(\text{Cl}^-)$, and eq 15 a way

Table II. Changes in Anion and Cation Solvating Power and Changes in Acceptor and Donor Properties of Solvents on Transfer from DMF at 25 °C (values in kJ g-ion⁻¹)

Solvent ^a	Registry no.	ϵ^b	Cation solvating power		Anion solvating power		
			+ 1.30 Δ (DN)	$-\Delta G_{tr}(K^+)^e$	+ 1.30 Δ (AN) ^b	$-\Delta G_{tr}(Cl^-)$	
1	DCE	107-06-2	10.1	>-35		+1	
2	<i>n</i> -Hexane	110-54-3	1.9	>-35 ^{i,k}	ca. -180 ^j	>-20 ^k	
3	MeNO ₂	75-52-5	36.7	-31	-31	+6	+14
4	PhNO ₂	98-95-3	34.8	-29		-2	
5	MeCN	75-05-8	36.0	-16	-19	+4	4
6	TMS	126-33-0	43.3	-15	-15		+4
7	Dioxane	123-91-1	2.2	>-15 ^k		>-6 ^k	
8	PC	2453-03-4	65.0	-15	-12	+3	+4
9	Me ₂ CO	67-64-1	20.7	-12	-11	-4 ₅	-11
10	H ₂ O	7732-18-5	78.5	-11	-9	+50	+46
11	MeOH	67-56-1	32.6	-10	-18	+32	+32
12	Ether	60-29-7	4.2	>-10 ^k		>-15 ^k	
13	DMF	68-12-2	36.7	0 ^g	0	0 ^g	0
14	NMePy	872-50-4	33.0	+1	+1	-4	-3
15	DMA	127-19-5	37.8	+2	+2	-4 ₅	-3
16	Me ₂ SO	67-68-5	46.7	+4	+3	+4 ₅	+6
17	Pyd	110-86-1	12.3	+8		-3	
18	HMPT [†]	680-31-9	29.6	+16	+8	-7	-13
19	NMeF	123-39-7	182.4			+21	+25
20	Me ₂ CHOH	67-63-0	18.3			+22 ₅	
21	EtOH	64-17-5	24.3		-25	+27	+25
22	HCONH ₂	75-12-7	109.5		-7	+31	+33
23	HOAc	64-19-7	6.3			+48	
24	CF ₃ CH ₂ OH	75-89-8	26.1		-45	+48 ^c	+56
25	CF ₃ CO ₂ H	76-05-1	8.3	>-35 ^k	>-45 ^h	<+115 ^d	
26	0.32 Me ₂ SO-H ₂ O					33 ^m	26 ^l
27	0.89 MeCN-H ₂ O					20 ^m	20 ⁿ
28	0.80 MeCN-H ₂ O					27 ^m	25 ⁿ
29	0.63 MeCN-H ₂ O					34 ^m	32 ⁿ
30	0.51 MeCN-H ₂ O					35 ^m	36 ⁿ
31	0.40 MeCN-H ₂ O					36 ^m	38 ₅ ⁿ
32	0.30 MeCN-H ₂ O					38 ^m	40 ⁿ
33	0.20 MeCN-H ₂ O					43 ^m	40 ⁿ
34	0.10 MeCN-H ₂ O					47 ^m	44 ⁿ

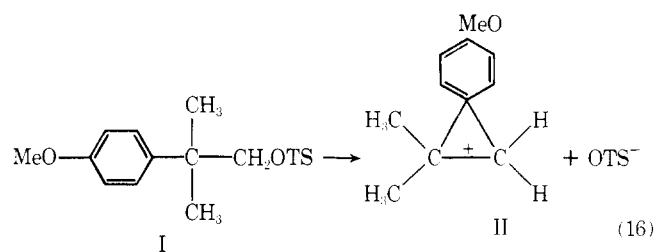
^a Abbreviations are: DCE, 1,2-dichloroethane; TMS, tetramethylene sulfone at 30 °C; PC, propylene carbonate; DMF, *N,N*-dimethylformamide; NMePy, *N*-methyl-2-pyrrolidinone; DMA, *N,N*-dimethylacetamide; Me₂SO, dimethyl sulfoxide; HMPT, hexamethylphosphoric triamide; NMeF, *N*-methylformamide. Solvent mixtures: numbers indicate mole fraction of organic solvent component. ^b Reference 12. ^c U. Mayer, private communication. ^d Maximum value, because acceptor number includes chemical shift for protonated Et₃PO averaged with chemical shift of CF₃CO₂H-OPEt₃ adduct. ^e Reference 22 and 23. ^f From $\Delta G_{tr}(AgCl)^{11,20} - \Delta G_{tr}(Ag^+)(TATB)$, Table 1 or ref 23. ^g The donor number of DMF is 26.6 and its acceptor number is 16.0. ^h Estimated from low dielectric constant and low basicity of this solvent. ⁱ Solvents which are weaker donors than 1,2-dichloroethane should have negative donor numbers. Assignment of DN = 0 in eq 11 therefore indicates a solvating power which is somewhat too high. ^j $\Delta G_{tr}(K^+)$ is 340 kJ g-ion⁻¹ for transfer from DMF to the gas phase.²² A simple Born calculation, using a dielectric constant of 1.9 for hexane, predicts $\Delta G_{tr}(K^+)$ of 180 kJ g-ion⁻¹ for transfer from DMF to hexane. ^k It seems unlikely that the donor-acceptor concept for predicting ion solvating power extends to these very low dielectric solvents. We expect weaker ion solvating power than predicted by donor and acceptor numbers. ^l Reference 2. ^m U. Mayer, W. Gerger, and V. Gutmann, *Monatsh. Chem.*, **108**, 489 (1977). ⁿ W. E. Waghorne, Ph.D. Thesis, Australian National University, Canberra, Australia, 1972.

of measuring acceptor numbers indirectly from rate constants in different solvents, should these not be otherwise available, and all three are related through eq 10 and 12.

In summary then, rates of S_N2 reactions between anions and molecules in polar solvents have tolerable linear free-energy relationships with the anion solvating properties and with the acceptor properties of the solvents as recorded in Table II. An example is illustrated in Figure 3 for reaction 6 of Table IV.

S_N1 Solvolysis. Two classical investigations of physical organic chemistry are the solvent effects on the rates of solvolysis of *tert*-butyl chloride and *p*-methoxyneophyl tosylate (eq 16). The solvolysis of *tert*-butyl chloride leads to the Grunwald-Winstein *Y* values^{27,28,29} and the solvolysis of *p*-methoxyneophyl tosylate (I) measures "solvent ionizing power".^{30,31} The subsequent work by Abraham^{3,15} on *tert*-butyl chloride has been particularly illuminating, as have the investigations of Schleyer and co-workers³¹ and Rudakov³² on this and related substrates. It is of interest to simplify these highly sophisticated and successful interpretations for the

benefit of nonspecialists, who are familiar with the principles of anions, cation, and molecule solvation, but not the language and concepts of the physical organic chemist. As noted, Fawcett and Krygowski⁸ have presented relationships which are closely related to ours, but we consider important new data points and discuss the implications in a somewhat different way.



***p*-Methoxyneophyl Tosylate.** There is an excellent linear free-energy relationship (eq 17) between $\Delta G_{tr}(Cl^-)$ at 25 °C

Table III. Sensitivities of Anions, Cations, and S_N2 Reactions to Solvent Transfer through High Dielectric Solvents at 25 °C. Values of *n* and *p* in eq 9–15 and 2

Anions ^c Y ⁻	Registry no.	<i>n</i> (eq 10)	<i>n</i> ' (eq 12 ^d)	Cations ^e M ⁺	Registry no.	<i>p</i> (eq 9)	<i>p</i> ' (eq 11 ^f)
F ⁻	16984-48-8	1.25	1.62	Zn ²⁺	23713-49-7	5.2	7.5
OAc ⁻	71-50-1	1.33	1.73	Cd ²⁺	22537-48-0	4.3	6.0
Cl ⁻	16887-00-6	1.00	1.30	Ba ²⁺	22541-12-4	3 ₃	4 ₅
Br ⁻	24959-67-9	0.74	1.00	Li ⁺	17341-24-1	2.1	2.9
N ₃ ⁻	14343-69-2	0.75	1.0	Na ⁺	17341-25-2	1.5	2.1
SCN ⁻	1111-68-8	0.35 ^a	0.45	K ⁺	24203-36-9	1.0	1.30
OTs ⁻	16722-51-3	0.3–0.4 ^g	0.4–0.5 ^{c, g}	Cs ⁺	18459-37-5	0.7	1.0
I ⁻	20461-54-5	0.3 ₅ –0.4 ^a	0.4–0.5	NMe ₄ ⁺	51-92-3	0.5	0.7
ClO ₄ ⁻	14797-73-0	0	0	Ph ₄ As ⁺	15912-80-8	0.25	0.3
BPh ₄ ⁻	4358-26-3	0.0 ₅	0.0 ₅				

Registry no. (RX)	Reactants RX + Y ⁻	<i>n</i> ' (eq 13 ^{b, c})	<i>n</i> (eq 14 ^{b, c})	<i>n</i> ' (eq 15 ^{b, d})
74-88-4	CH ₃ I + SCN ⁻	1.0 ^a	0.35	0.45
	CH ₃ I + Br ⁻	1.0	0.7	1.0
	CH ₃ I + Cl ⁻	1.0	1.0	1.30
74-83-9	CH ₃ Br + SCN ⁻	1.0 ^a	0.35	0.45
	CH ₃ Br + Cl ⁻	0.80	0.80	1.0
109-65-9	<i>n</i> -BuBr + N ₃ ⁻	0.73	0.55	0.72
80-48-8	CH ₃ OTs + N ₃ ⁻	0.50	0.36	0.54
350-46-9	4-NO ₂ C ₆ H ₄ F + N ₃ ⁻	1.0	0.75	1.0
636-98-6	4-NO ₂ C ₆ H ₄ I + N ₃ ⁻	1.0	0.75	1.0
709-49-9	2,4-(NO ₂) ₂ C ₆ H ₃ I + SCN ⁻	1.0 ^a	0.35	0.45
	2,4-(NO ₂) ₂ C ₆ H ₃ I + Cl ⁻	1.0	1.0	1.30

^a Significant deviations from the appropriate equations occur for some solvents because of difficulties in measuring solubilities of AgI and AgSCN.¹⁸ ^b Values of $\Delta G_{tr}^{\ddagger}(S_{N2})$ calculated from ref 2. ^c Values of $\Delta G_{tr}(Y^-)$ from Table I or from $\Delta G_{tr}(Ag^+) + \Delta G_{tr}(Y^-)$ ^{11,20} – $\Delta G_{tr}(Ag^+)$ (TATB), Table I. ^d Values of $\Delta(AN)$ from acceptor numbers in Table II. ^e Values of $\Delta G_{tr}(M^+)$ from ref 11 or 23. ^f Donor numbers from Table II. ^g Only three data points available: cf. R. Alexander, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.*, **89**, 3703 (1967).

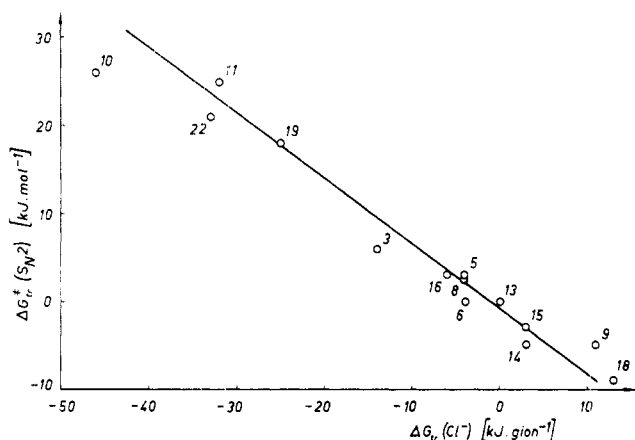


Figure 3. Relationship between transfer free energy of activation $\Delta G_{tr}^{\ddagger}(S_{N2})$ and anion solvating power of solvents for transfer of the S_NAr reaction between azide ion and 4-fluoronitrobenzene at 25 °C. Plot of the equation $\Delta G_{tr}^{\ddagger}(S_{N2}) = -0.75\Delta G_{tr}(Cl^-)$, cf. eq 14 and Table IV.

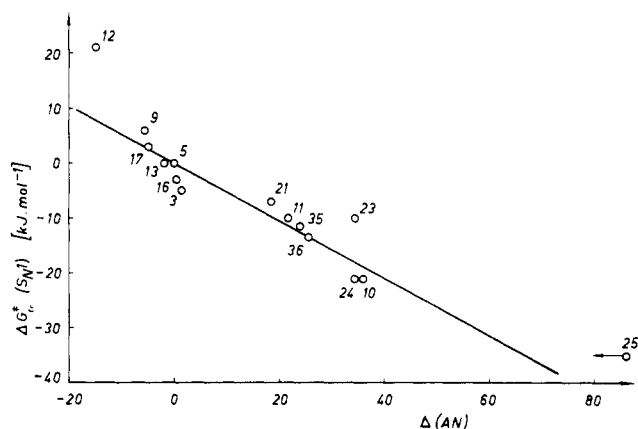


Figure 4. Relationship between transfer free energy of activation and solvent acceptor properties for solvolysis of *p*-methoxyneophyl tosylate at 75 °C. Plot of the eq 18 $\Delta G_{tr}^{\ddagger}(S_{N1}) = -0.52\Delta(AN)$; cf. Table V. No. 35: mole fraction EtOH in mixture with water = 0.55. No. 36: mole fraction MeOH in mixture with water = 0.64.

(Table II) and the transfer free energy of activation for solvolysis of *p*-methoxyneophyl tosylate at 75 °C (Table V). Even water tolerably satisfies the relationship. The value of *n* is 0.40.

$$\Delta G_{tr}^{\ddagger}(S_{N1}) = n\Delta G_{tr}(Cl^-) \quad (17)$$

A corollary of eq 10, 12, and 17 is given by eq 18. As shown in Figure 4 and Table V there is a good correlation between acceptor numbers of pure solvents and alcohol–water mixtures and solvolysis rates ($\Delta G_{tr}^{\ddagger}(S_{N1})$) of *p*-methoxyneophyl tosylate. The value of *n*' is 0.52 as required by the special case of eq 12, $\Delta G_{tr}(Cl^-) = -1.30\Delta(AN)$, and by *n* = 0.4 in eq 17. The

use of acceptor numbers allows us to introduce extra data points for which $\Delta G_{tr}(Cl^-)$ are not available. However these are all for solvents of low dielectric constant, i.e., acetic acid (6.3), ether (4.2), pyridine (12.3), and trifluoroacetic acid (8.3). Substantial positive deviations (up to +13 kJ mol⁻¹) from the requirements of eq 18 are observed in three of the solvents, but pyridine is well correlated in a relationship covering 56 kJ mol⁻¹ in $\Delta G_{tr}^{\ddagger}(S_{N1})$.

$$\Delta G_{tr}^{\ddagger}(S_{N1}) = -n'\Delta(AN) \quad (18)$$

Unlike the good correlations with chloride anion solvating power and acceptor number, there is no meaningful rela-

Table IV. Correlation of Solvent Effects on S_N2 Rates through eq 2, 13, 14 or 15. Transfer at 25 °C in kJ mol⁻¹ from Dimethylformamide of Reactions RX + Y⁻ → RY + X⁻

Solvent ^a	$\Delta G_{tr}(RX)^b$	$\Delta G_{tr}^{\ddagger}(S_N2)^b$ (obsd)	$-n''\Delta G_{tr}(Y^-)^g$ (eq 13)	$-n\Delta G_{tr}(Cl^-)^e$ (eq 14)	$+n'\Delta(AN)^e$ (eq 15)	$\Delta G_{tr}^{\ddagger}(S_N2)$ (eq 2a)	$\Delta G_{tr}^{\ddagger}(S_N2)$ (eq 2b)
Reaction 1: RX = CH ₃ I; Y ⁻ = Cl ⁻ ; n'' = 1.0; n = 1.0; n' = 1.30							
H ₂ O	11	35		46	50	35	39
HCONH ₂	6	27		33	31	27	25
DMF	0	0		0	0	0	0
DMA	0	-3		-3	-3	-3	-3
MeCN	1	7		4	4	3	3
NMePy	-1	-6		-3	-3 ₅	-2	-2 ₅
MeNO ₂	2	10		14	6	12	4
Me ₂ CO	-2	0		-11	-4 ₅	-9	-2 ₅
MeOH	3	34		32	33	29	30
NMeF		24 ₅ ^d		25	21		
C ₂ H ₄ Cl ₂		5 ^c			1		
Reaction 2: RX = CH ₃ I; Y ⁻ = Br ⁻ ; n'' = 1.0; n = 0.75; n' = 1.00							
CF ₃ CH ₂ OH		31 ^f	41	41	37		
H ₂ O	11	26	34	34	39	23	28
MeOH	3	24	23	24	25	21	22
HCONH ₂	6	20	24	24	24	18	18
EtOH	2	20 ₅ ^f	15	18 ₅	21	17	19
MeCN	1	7 ^f	3	3	3	2	2
DMF	0	0	0	0	0	0	0
Me ₂ CO	-2	-5	-8	-8	-3 ₅	-6	-1 ₅
NMePy	-1	-7	-1	-2	-3	-1	-2
Reaction 3: RX = CH ₃ I; Y ⁻ = SCN ⁻ ; n'' = 1.0; n = 0.35; n' = 0.45							
H ₂ O	11	14	16	16	17 ₅	5 ^j	6.5 ^j
MeOH	3	13	10	11	11	8 ^j	8 ^f
HCONH ₂	6	10	12	11	11	5 ^j	5 ^j
NMeF		7 ₅		8 ₅	7		
MeNO ₂	2	5	7	5	2	3	0
MeCN	1	5	3	1 ₅	1	0	0
DMF	0	0	0	0	0	0	0
DMAC	0	-2	-1	-1	-1	-1	-1
PC		4 ^f	7	2	1		
Me ₂ CO	-2	-2		-4	-2	-2	0
NMePy	-1	-7	-3	-1	-1	0	0
Me ₂ SO	0	2 ^f	+8	+2	+1 ₅	2	1 ₅
0.70 Me ₂ SO-H ₂ O	4 ₅	7 ₅	8		6		1 ₅
0.32 Me ₂ SO-H ₂ O	7	8	8 ₅	9	15 ₅	2	4 ₅
Reaction 4: RX = n-BuBr; Y ⁻ = N ₃ ⁻ ; n'' = 0.73; n = 0.55; n' = 0.72							
MeOH	1	19	17 ₅	18	18	17	17
H ₂ O	>15	15	25	25	28	<10	<13
HCONH ₂	4	13	17	18	17	14	13
TMS		4 ₅		2			
Me ₂ SO	1	2	8	3	2	2	1
DMF	0	0	0	0	0	0	0
MeCN	-0 ₅	-2	4	2	2	2 ₅	2 ₅
DMAC	0	-3	-1	-2	-2	-2	-2
Me ₂ CO	0	-3	-7	-6	-2 ₅	-6	-2 ₅
HMPT	-1 ₅	-5	-9	-7	-4	-6	-2 ₅
Reaction 5: RX = 2,4-(NO ₂) ₂ C ₆ H ₃ I; Y ⁻ = SCN ⁻ ; n'' = 1.0; n = 0.35; n' = 0.45							
HCONH ₂	ca.9 ^h	11	12	11	11	2 ^j	2 ^j
MeOH	>6 ^h	10	10	11	11	<5 ^j	<5 ^j
Me ₂ SO		3	8 ⁱ	2	1 ₅		
MeNO ₂		2	7	5	2		
MeCN		1	3	1	1		
DMF	0	0	0	0	0	0	0
TMS		0		1			
NMePy		-2	-3	-1	-1		
DMAC		-2	-1	-1	-1		
Me ₂ CO		-6		-4	-2		
Reaction 6: RX = 4-NO ₂ C ₆ H ₄ F; Y ⁻ = N ₃ ⁻ ; n'' = 1.0; n = 0.75; n' = 1.0							
H ₂ O	>15 ^h	26 ⁿ	35	35	39	<20 ^j	<24 ^j
MeOH	7 ^h	25	24	24	25	17 ^j	18 ^j
HCONH ₂	9 ^h	21	23	25	24	16 ^j	15 ^j
NMeF		18 ^{l,m}		19	16		
MeNO ₂		6 ⁿ	10	10	4 ₅		
Me ₂ SO	0.5 ^h	3 ⁿ	11	4 ₅	3	4 ^j	2 ₅ ^j
MeCN	4 ₅ ^h	3 ⁿ	6	3	3	-1 ₅ ^j	-1 ₅ ^j

Table IV (Continued)

Solvent ^a	$\Delta G_{\text{tr}}(\text{RX})^b$	$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}2)^b$ (obsd)	$-n''\Delta G_{\text{tr}}(\text{Y}^-)^g$ (eq 13)	$-\Delta G_{\text{tr}}(\text{Cl}^-)^e$ (eq 14)	$+n'\Delta(\text{AN})^e$ (eq 15)	$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}2)$ (eq 2a)	$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}2)$ (eq 2b)
Reaction 6 (Continued)							
PC		2 ₅ ⁿ	6	3	2		
PhCN		1 ^l			0		
PhNO ₂		0 ^l			-1		
DMF	0 ^h	0	0	0	0	0	0
TMS		0 ⁿ		3			
DMAC		-3	-1	-2	-2		
Me ₂ CO		-5	-9	-8	-3 ₅		
NMePy	-1 ₅ ^h	-5	-6	-2	-3	-0 ₅ ^j	-1.5 ^j
HMPT	-2 ^h	-9 ⁿ	-13	-7	-5	-5 ^j	-3 ^j

^a Abbreviations as in Table II. ^b Reference 2, unless stated otherwise. ^c Reference 40. ^d A. J. Parker, *J. Chem. Soc.*, 1328 (1961). ^e Table II. ^f Reference 20. ^g Table I unless stated otherwise. ^h Estimated from ΔG_{tr} for 4-NO₂C₆H₄I and 2,4-(NO₂)₂C₆H₃Cl, ref 2. ⁱ $\Delta G_{\text{tr}}(\text{Y}^-)$ is uncertain; see Table I. ^j These equations are not expected to apply to these reactions; see text. ^k Both 4-NO₂C₆H₄F and 2,4-(NO₂)₂C₆H₃Cl (ref 2) have solubilities >1 M in DMF and <10⁻³ M in water at 25 °C. $\Delta G_{\text{tr}}(\text{RX})$ is >15 kJ mol⁻¹. ^l J. Miller and A. J. Parker, *J. Am. Chem. Soc.*, **83**, 117 (1961). ^m Extrapolated from a rate constant measured at 100 °C, assuming same activation energy as for reaction in formamide. ⁿ Reference 6.

Table V. Correlation of Solvent Effects on Rate of Solvolysis of *p*-Methoxyneophyl Tosylate^k (ROT) at 75 °C: Transfer from Acetonitrile

Solvent ^a	$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$ (obsd)	$-0.52\Delta(\text{AN})^f$ (eq 18)	$0.40\Delta G_{\text{tr}}(\text{Cl}^-)^f$ (eq 17)
CF ₃ CO ₂ H	-35 ^d	-45 ^g	
CF ₃ CH ₂ OH	-21 ^e	-18	-21
H ₂ O	-21 ^{b,c}	-19	-17
MeOH	-10 ^c	-12	-11
HOAc	-10 ^c	-18	
EtOH	-7 ^c	-9 ₅	-8
Me ₂ SO	-3 ^c	0	-1
MeNO ₂	-5 ^c	-1	-4
DMF	0 ^c	1 ₅	2
MeCN	0 ^c	0	0
Pyd	3 ^c	2	
Me ₂ CO	6 ^c	3	6
Ether	21 ^c	>8 ^h	
0.64 MeOH-	-13 ⁱ	-13 ^j	
H ₂ O			
0.55 EtOH-	-11 ₅ ⁱ	-12 ₅ ^j	
H ₂ O			

^a Abbreviations as in Table II, pyd is pyridine. ^b Approximate value, extrapolated from water-solvent mixtures. ^c Reference 30. ^d Estimated from solvolysis of neophyl tosylate in this solvent: A. F. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 6546 (1968). ^e Estimated from solvolysis of 2-adamantyl tosylate, ref 31. ^f Table II. ^g See footnote d, Table II. ^h Footnote k, Table II. ⁱ Calculated from rate constants at 25 and 50 °C given in ref 30. ^j See footnote m, Table II. ^k Registry no.: 59024-80-5.

relationship such as eq 19 between $\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$ for these solvolyses and the cation solvating power of the solvents (Table II). As shown by Fawcett and Krygowski,⁸ the dependence of these rates on solvent donor properties is negligible.

$$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1) = p\Delta G_{\text{tr}}(\text{K}^+) = -p'\Delta(\text{DN}) \quad (19)$$

Solvolysis of *p*-methoxyneophyl tosylate is always faster in the significantly stronger anion solvating solvents (e.g., trifluoroethanol, trifluoroacetic acid) of a set of solvents, irrespective of cation solvating power. Instructive comparisons from Table V are: the similar values of $\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$ between CH₃NO₂ and Me₂SO, which are two solvents of very different cation solvating, but similar anion solvating properties (Table II); faster solvolysis in ethanol than DMF; and similar rates of solvolysis in water and trifluoroethanol (similar AN) despite a difference of 35 kJ g-ion⁻¹ in their ability to solvate K⁺ (Table II).

To summarize, rates of solvolyses of *p*-methoxyneophyl tosylate in solvents of high polarity have a linear free-energy relationship with the anion solvating properties, as measured by $\Delta(\text{AN})$ or $-\Delta G_{\text{tr}}(\text{Cl}^-)$ of the solvents. In the language of the physical organic chemists, Figure 4 and Table V establish that electrophilic solvation of the leaving group, rather than solvent ionizing power, is the major factor in determining differences in rates of solvolysis of *p*-methoxyneophyl tosylate. These are limiting solvolyses, with no detectable nucleophilic participation by the solvent. We cannot agree that it is not necessary to account explicitly for electrophilic (anionic) solvation of the leaving group in these solvolysis reactions³¹ and recall the original Hughes-Ingold formulation³³ of an S_N1 reaction. "S_N1 reactions involve a rate-determining ionization to a cationic intermediate. The solvent functions largely in an electrophilic manner (as an acceptor) to heterolyze the C-X bond and solvate the anion. No covalent interaction between the solvent and cation is required." Certainly this solvolysis fits that description.

***tert*-Butyl Chloride.** $\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$ for *tert*-butyl chloride solvolysis, as measured by the rate of production of HCl, is analyzed in Table VI. The linear free-energy relationship (eq 17) is less satisfactory than it was for *p*-methoxyneophyl tosylate. Rates of solvolysis by water and formamide are now much faster than required by eq 17. Weak cation solvators of very different anion solvating properties, such as ethanol, methanol, trifluoroethanol, nitromethane, acetonitrile, and acetone, fit a linear relationship of slope 0.5 in eq 17. However solvolysis of *tert*-butyl chloride by solvents which are very strong cation solvators (Table II), such as DMF, *N*-methylpyrrolidine, DMAC, and Me₂SO, are a little faster than required by eq 17.

As noted, eq 18 is a corollary of eq 10, 12, and 17, so like eq 17 it gives a tolerable correlation between solvent acceptor numbers and $\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$ for solvolysis of *tert*-butyl chloride in solvents of high dielectric constant, other than water. The value of n' is 0.65 in Table VI. The use of acceptor numbers gives much the same deviations as eq 17, but allows inclusion of data points, for ether (4.2), dioxane (2.2), heptane (1.9), nitrobenzene (35), isopropyl alcohol (18.3), acetic acid (6.3), and trifluoroacetic acid (8.3). Many of these are low dielectric solvents (values in parentheses) so only maximum values of their anion solvating power can be estimated from $\Delta(\text{AN})$ (Table II). The low dielectric solvents (<10) all actually solvolyze *tert*-butyl chloride *more slowly* than predicted by solvent acceptor numbers in eq 18. The slower than predicted rates are observed whether the low dielectric solvents are poor acceptors and donors, like heptane, strong donors but weak

Table VI. Correlation of Solvent Effects on Rates of Solvolysis of *tert*-Butyl Chloride^p and *tert*-Butyl Bromide^q at 25 °C. Transfer from Acetonitrile in kJ mol⁻¹ (*t*-BuCl) or DMF (*t*-BuBr)

$$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1) = p\Delta G_{\text{tr}}(\text{K}^+) + n\Delta G_{\text{tr}}(\text{Cl}^-) - \Delta G_{\text{tr}}(t\text{-BuX}) \quad (1a)$$

$$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1) = -p'\Delta(\text{DN}) - n'\Delta(\text{AN}) - \Delta G_{\text{tr}}(t\text{-BuX}) \quad (1b)$$

Solvent ^a	Reaction: <i>t</i> -BuX = <i>t</i> -BuCl; <i>p</i> = 0.20; <i>p'</i> = 0.28; <i>n</i> = 0.50; <i>n'</i> = 0.65					
	$\Delta G_{\text{tr}}(t\text{-BuX})^b$	$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$ (obsd ^c)	$n\Delta G_{\text{tr}}(\text{Cl}^-)^i$ (eq 17)	$-n'\Delta(\text{AN})^i$ (eq 18)	$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$ (eq 1a)	$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$ (eq 1b)
H ₂ O	18	-41 ^c	-21	-23	-41	-45
CF ₃ CO ₂ H		-32 ^h		<-56 ^g		<-52
CF ₃ CH ₂ OH		-27 ^h	-26	-22	>-22	
HCONH ₂	4 ^j	-25 ^c	-14 ₅	-13 ₅	-20 ₅	-21.5
MeOH	1	-15 ^c	-14	-14 ₅	-15	-16.5
HOAc	0	-12 ^c		-22		<-19
EtOH	0	-9 ^c	-10 ₅	-12	-9 ₅	
Me ₂ CHOH	0	-6 ^c		-9		-10
Me ₂ SO	1	-5 ^d	-1	0	-6	-5
MeNO ₂	1	-4 ^d	-5	-1	-3	2
DMF	-1	-1 ^d	2	2	-1	-1
DMA	-1 ^k	-0 ₅ ^d	3 ₅	4	-1	2
MeCN	0	0 ^d	0	0	0	0
NMePy	-1	1 ₅ ^d	3 ₅	4	0 ₅	2
PhNO ₂	-2	6 ^d	3	3	8	5
Me ₂ CO	-2	8 ^d	7 ₅	4	8 ₅	5 ₅
Dioxane	-2	12 ^d		>5 ^f		>8
Ether	-3	23 ^d		>10 ^f		>12
<i>n</i> -Heptane	-3	42 ^d		>13 ^f		>21
0.2 MeOH-H ₂ O	12 ^l	-35 ^m		-21 ⁿ		-34 ^o
0.4 MeOH-H ₂ O	8 ^l	-29 ₅ ^m		-19 ⁿ		-28 ^o
0.6 MeOH-H ₂ O	6 ^l	-24 ^m		-17 ⁿ		-24 ^o
0.8 MeOH-H ₂ O	3 ₅ ^l	-19 ^m		-16 ⁿ		-20 ₅ ^o

Reaction: *t*-BuX = *t*-BuBr; *p* = 0.20; *p'* = 0.28; *n* = 0.35; *n'* = 0.45 from DMF

	$\Delta G_{\text{tr}}(t\text{-BuX})$	$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$	$n\Delta G_{\text{tr}}(\text{Cl}^-)$	$-n'\Delta(\text{AN})$	$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$	$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$
H ₂ O	22	-32 ^b	-12	-17 ₅	-32	-37.5
CF ₃ CH ₂ OH		-18 ^e	-14	-17	>-8	
MeOH	3	-7 ^b	-8	-11	-7	-12
EtOH	1	-2 ^b	-5	-9 ₅	-1	
DMF	0	0 ^b	0	0	0	0
DMA	0 ^k	0 ^b	0	1	0	1
NMePy	0	2 ^b	1	1	1	1
Me ₂ CO	-0 ₅	7 ^b	3	1 ₅	6 ₅	3 ₅

^a Abbreviations as in Table II. ^b Reference 3. ^c Reference 29. ^d Reference 15. ^e F. L. Scott, *Chem. Ind.*, 224 (1959). ^f Recorded acceptor numbers for these low dielectric solvents give maximum estimates of their anion solvating power only (see text and Table II). ^g See footnote d, Table II. ^h Reference 31. ⁱ From Table II. ^j Estimated from *n*-BuBr, ref 2. ^k Estimated from DMF. ^l Interpolated from M. H. Abraham and G. F. Johnston, *J. Chem. Soc. A*, 1610 (1971) after conversion to mole fraction scale. ^m Interpolated from ref 29. ⁿ See footnote *m*, Table II. ^o Assuming DN = constant \approx 18 for MeOH-H₂O mixtures. ^p Registry no.: 507-20-0. ^q Registry no.: 507-19-7.

Table VII. Analysis of Solvent Effects on Rate of Solvolyses of *trans*-4-*tert*-Butylcyclohexyl Tosylate^f (ROT_s) at 75 °C. Transfer from Acetonitrile in kJ mol⁻¹

Solvent ^a	$\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$ (obsd)	$-0.5\Delta(\text{AN})^e$ (eq 18)	$p\Delta G_{\text{tr}}(\text{K}^+) - \Delta G_{\text{tr}}(\text{ROT}_s)$ (eq 1)	$0.4\Delta G_{\text{tr}}(\text{K}^+)$
CF ₃ CO ₂ H	-29 ^d	<-43	<14	>10
CH ₃ CO ₂ H	-18 ^d	-16	-2	
Me ₂ SO	-9 ^b	0	-9	-9
EtOH	-7 ^c	-8	1	2
DMF	-4 ^b	+3	-7	-8
MeNO ₂	-1 ^b	0	-1	+5
MeCN	0 ^b	0	0	0
Me ₂ CO	5 ^b	4	1	-3

^a Abbreviations as in Table II. ^b Reference 42. ^c S. Winstein and N. J. Hollness, *J. Am. Chem. Soc.*, 77, 5562 (1955). ^d Reference 43. ^e Acceptor number from Table II. ^f Registry no.: 7453-05-6.

acceptors, like ether and dioxane, or very strong acceptors but weak donors, like acetic acid and trifluoroacetic acid.

For the same solvents, eq 17 is a little more satisfactory than eq 18.

Other Substrates. $\Delta G_{\text{tr}}^{\ddagger}(\text{S}_{\text{N}}1)$ for solvolysis of *tert*-butyl bromide is also analyzed in Table VI and *trans*-4-*tert*-butylcyclohexyl tosylate is analyzed in Table VII. Equation 18 is clearly not acceptable as describing solvent effects on

rates of solvolysis of *trans*-4-*tert*-butylcyclohexyl tosylate in DMF and Me₂SO. The solvolyses of *tert*-butyl bromide fit eq 18 in much the same indifferent way as do those of *tert*-butyl chloride, but n' in eq 18 is of course less (0.45) because the larger bromide ion is less responsive to solvent anion solvating properties than is the developing chloride ion in *t*-BuCl[±].

Discussion

It is of interest to examine why we obtain the linear relationships eq 13, 14, 15, 17, and 18 between rates, $\Delta G_{tr}(Y^-)$, $\Delta G_{tr}(Cl^-)$, and acceptor number for several S_N2 and S_N1 reactions in different solvents.³⁴ Even more interesting are the reasons for the deviations which we have noted: i.e., reaction in water and formamide sometimes but not always faster than required by the relationships; solvolyses in strong cation solvators like DMF and Me₂SO sometimes but not always faster than predicted; and much slower solvolyses in low dielectric solvents with a large range of donor and acceptor properties than required by the relationships.

S_N2 Reactions. Rates of S_N2 reactions in different solvents are determined by the three transfer free energies of eq 8. Two simplifications are possible.

First, if the transition state anion, YRX^{-±}, is large with low surface charge, as for the S_NAr reaction of azide ion with 4-fluoronitrobenzene, and if RX is of similar structure and size to YRX^{-±} (e.g., 4-fluoronitrobenzene),^{2,6} then we use an assumption, familiar for nonaqueous solvent chemists, that $\Delta G_{tr}(YRX^{-\pm}) = \Delta G_{tr}(RX)$.^{20,35} This "transition state" assumption is valid for formamide as well as other polar solvents of high dielectric constant, but may break down for solvents of low dielectric constant and for water.²⁰ The equality given above is equivalent to assumptions like $\Delta G_{tr}(Ph_4B^-) = \Delta G_{tr}(Ph_4C)$ ²⁰ $\Delta G_{tr}(I_3^-) = \Delta G_{tr}(I_2)$ ³⁵ and is conceptually related to the ferrocene assumption,³⁶ the bis(biphenyl)chromium assumption,³⁷ and the cobaltocene assumption,³⁶ which are of the form $\Delta G_{tr}(M^+) = \Delta G_{tr}(M^0)$. The "transition-state assumption",³⁵ given above, reduces eq 8 to $\Delta G_{tr}^\ddagger(S_N2) = -\Delta G_{tr}(Y^-)$ as observed for reactions 3, 5, and 6 in Table IV, over a wide range of solvents. This type of situation is a special case of eq 13 ($n'' = 1$) and is common for aromatic nucleophilic substitution reactions, as shown by their n'' values of unity in Table III and correlations for formamide in Table IV, reactions 5 and 6. It is less common for substitution at saturated carbon, but reactions of iodomethane with large anions such as thiocyanate (reaction 3, Table IV) approximate to it.² In these cases, eq 13-15 give a much better correlation than eq 2 for water and formamide as shown in Table IV.

In the second simplification we have the more general case of eq 13. If RX is not large (e.g., CH₃Cl) or if for various reasons the S_N2 transition state is loose (N₃CH₃OTS^{-±})²⁶ or if its surface charge is significant (N₃BuBr^{-±}), then $\Delta G_{tr}(RX)$ does not equal $\Delta G_{tr}(YRX^{-\pm})$ and the two terms must be considered.² The transition state (YRX^{-±}) is an anion, but is larger and has less surface charge than Y⁻. Thus it is subject to eq 10 and 12, corresponding less strongly to solvent transfer but in the same way as does Y⁻. This corollary is expressed in eq 20, which leads from eq 8 to eq 21 and 22.

$$\Delta G_{tr}(YRX^{-\pm}) = n' \Delta G_{tr}(Y^-) \quad (20)$$

$$\Delta G_{tr}^\ddagger(S_N2) = n' \Delta G_{tr}(Y^-) - \Delta G_{tr}(Y^-) - \Delta G_{tr}(RX) \quad (21)$$

$$\Delta G_{tr}^\ddagger(S_N2) = -n'' \Delta G_{tr}(Y^-) - \Delta G_{tr}(RX) \quad (22)$$

$$\text{where } n'' = 1 - n'$$

Equation 2 is a corollary of eq 22, through eq 10 and 12.

In eq 20, n' values are less than unity and decrease as YRX^{-±} decreases in surface charge (Table III) relative to Y⁻. Thus n'' in eq 22 is also less than unity, but *increases* toward unity as YRX^{-±} decreases in surface charge. For an anion

YRX^{-±} of comparable low surface charge to ClO₄⁻, as shown in Table III, n' in eq 20 will be zero. Thus n'' in eq 22 and eq 13 will be unity. An example is reaction 1 in Table IV. It is important to note that reaction 1 in Table IV is *not* the same situation as discussed above for reaction 3 in Table IV, where n'' was unity because of the equality of $\Delta G_{tr}(RX)$ and $\Delta G_{tr}(YRX^{-\pm})$. Although n'' is unity in both cases, the difference lies in the need or otherwise to include $\Delta G_{tr}(RX)$ for transfer to water or formamide in the correlation, i.e., to use eq 2 and 22 or eq 13.

For transfer of the monofunctional type of uncharged reactant RX considered here through solvents other than water and to a lesser extent formamide, $\Delta G_{tr}(RX)$ is often negligible (± 2 kJ mol⁻¹),² as shown in Tables IV and VI. If this term is negligible in eq 22, the relationship reduces to eq 13 which, as illustrated for all reactions in Table IV, gives an acceptable approximate linear free-energy relationship for many S_N2 reactions in many solvents. As noted, if eq 3 is valid, then eq 14 and 15 follow as corollaries, via eq 10 and 12, and the success of these relationships is explained.

For transfer to water and formamide, $\Delta G_{tr}(RX)$ in eq 22 is significantly positive (Table IV). This is because hydrophobic, weakly polar species RX are more weakly solvated in highly structured solvents like water and formamide than by other solvents. Solvation of such species in water is by a mechanism known as solvation of the second kind.^{11,25,38} Less structured solvents, like DMF, CH₃CN, and methanol, do not use this mechanism and solvate RX more strongly and to a comparable extent (ΔG_{tr} is ± 2 kJ mol⁻¹), so that transfer between them involves little change in free energy.¹¹

If the transition state anion (YRX^{-±}) has significant negative surface charge, localized for example on Y and X, then its solvation by water, at least in the region of Y and X, is different from solvation of RX. It is solvation of the first kind^{11,38} and so $\Delta G_{tr}(YRX^{-\pm})$ is usually more negative than $\Delta G_{tr}(RX)$ on transfer to water. Thus the deviations from eq 13, 14, or 15, shown by reactions 1, 2, and 4 in Table IV, for transfer to water and formamide are explained. For transfer of these reactions to water and to some extent formamide, eq 22 or its corollary eq 2 gives a much better correlation of rates, which are otherwise faster than predicted by eq 13 or by its corollaries, eq 14 and 15. As noted, eq 13-15 give a better correlation of rates than eq 2 for reactions 3, 5, and 6 in water and formamide.

For a variety of reasons,^{3,32,33,39} the transition states for highly endoenergetic S_N1 ionizations are regarded as highly dipolar species, having a cationic and anionic center. They have some of the features of the products of ionization, i.e., of a carbonium ion and an anion. Although not implying that the transition state is a fully solvated cation and anion or an ion pair, we expect that the cationic portion of RX[±] will be solvated according to the cation solvating power of the solvent. The anionic portion will be solvated according to the anion solvating power of the solvent. As noted, ΔG_{tr} for cationic centers responds to a solvent transfer as indicated by the linear relationship eq 9 and 11, and anionic centers respond to solvent transfer as indicated by eq 10 and 12. Thus $\Delta G_{tr}(RX^\pm)$ will be given by the sum of $p\Delta G_{tr}(K^+) + n\Delta G_{tr}(Cl^-)$, or of $-p'\Delta(DN) - n'\Delta(AN)$. The relationship of eq 1 to eq 7 is now apparent.

In eq 1 the sensitivity to solvent transfer, p , n , p' , and n' , will be less than for the corresponding real cations and anions because the charged centers in this dipolar transition state are not fully solvated or developed ions. The sensitivity parameters tell us much about mechanism.

(A) *p*-Methoxyneophyl Tosylate. In the case of solvolysis of *p*-methoxyneophyl tosylate, Table V and Figure 4, we encounter a special case of eq 1 which could also be written as eq 23, since $p\Delta G_{tr}(K^+) = p''\Delta G_{tr}(R^+) = -p'\Delta(DN)$ through

eq 9 and 11. In eq 23, R^+ is the carbonium ion II.

$$\Delta G_{tr}^\ddagger(S_{N1}) = p'' \Delta G_{tr}(R^+) + n \Delta G_{tr}(Cl^-) - \Delta G_{tr}(RX) = p'' \Delta G_{tr}(R^+) - n' \Delta(AN) - \Delta G_{tr}(RX) \quad (23)$$

The bridged hydrophobic carbonium ion II has very low surface positive charge and is of comparable large size to the hydrophobic reactant molecule, *p*-methoxyneophyl tosylate (RX).³⁰ Its small positive surface charge means that cation solvating power is a negligible factor in determining its ΔG_{tr} through many solvents of dielectric constant 20–100 (p in eq 9 is small as for Ph_4As^+),²⁵ but again like $Ph_4As^{+11,25}$ its bulk and hydrophobic properties are significant factors in determining a large positive $\Delta G_{tr}(RX^\ddagger)$ for transfer to water. Thus we have a situation like that for the ferrocene–ferricinium couple,³⁶ the bis(biphenyl)chromium(I)–bis(biphenyl)chromium(0) couple,³⁷ and the cobaltocene–cobalticene couple,³⁶ which have been used by electrochemists to estimate $\Delta G_{tr}(\text{ion})$ from $\Delta E_{1/2}$ values. The ferrocene-like assumptions that $\Delta G_{tr}(M^0) = \Delta G_{tr}(M^+)$ have proved quite successful.^{10,36,37} For the same reasons that lead to the ferrocene assumption, we assume that $p'' \Delta G_{tr}(R^-) = \Delta G_{tr}(RX) = \Delta G_{tr}(R^+)$, where R^+ is cation II and RX is *p*-methoxyneophyl tosylate. Thus eq 23 reduces to eq 17 and 18 and the excellent relationship shown in Table V and Figure 4 for transfer between high dielectric solvents, including water, is explained.

It remains to be explained why eq 18 predicts faster solvolyses of *p*-methoxyneophyl tosylate than are observed in solvents of dielectric constant <10 . The full implications of ferrocene-like assumptions that $\Delta G_{tr}(M^0) = \Delta G_{tr}(M^+)$ need to be appreciated. The assumption has proved successful for transfer through solvents of dielectric constant 25–60, where $\Delta(1/\epsilon)_{tr}$ is 0–0.024, and thus changes in "Born-like solvation"²⁵ are negligible. However Born-like solvation can account for $>90\%$ of the solvation energy of an ion on transfer from gas phase to high dielectric solvents.²⁵ Thus we do not believe that $\Delta G_{tr}(M^+) = \Delta G_{tr}(M^0)$ for transfer from solvents of dielectric constant >25 to solvents of $\epsilon < 5$. Born calculations suggest that for such a transfer (where $\Delta(1/\epsilon)_{tr}$ is >0.16) $\Delta G_{tr}(M^+)$ is at least 20 kJ g-ion⁻¹, even for transfer of large cations of low surface charge, like ferricinium and Ph_4As^+ .²⁵ The similar solubilities of large polar molecules like ferrocene, *tert*-butyl chloride (Table VI), and 4-iodonitrobenzene² in dipolar aprotic solvents of $\epsilon > 25$ and in ether, hexane, and dioxane of $\epsilon < 5$ make it obvious that $\Delta G_{tr}(RX)$ and $\Delta G_{tr}(M^0)$ are $< \pm 5$ kJ mol⁻¹. Thus $\Delta G_{tr}(M^+)$ is greater than $\Delta G_{tr}(M^0)$ for transfer from high to very low dielectric solvents and the assumption which reduces eq 23 to eq 18 breaks down for such transfers. Then $\Delta G_{tr}^\ddagger(S_{N1})$, as observed, is more positive (i.e., solvolysis is slower) than predicted by eq 17 and 18 in Table V for solvolysis in ether, acetic acid, and trifluoroacetic acid.

The problem is accentuated by uncertainties as to whether acceptor numbers fully reflect the poor anion solvating power of very low dielectric solvents (Table II), so that other types of correlation may be more successful for such solvents.¹⁵

Despite these difficulties, three points should be emphasized: eq 17 and 18 correlate rates of this solvolysis to within 3 kJ for 10 of the 13 solvents in Table V, covering 27 kJ mol⁻¹ in $\Delta G_{tr}^\ddagger(S_{N1})$. It is notable that eq 18 correlates solvolysis in pyridine, a solvent of only moderate dielectric constant (12.3) and a strong cation solvator of high donor number. Despite its low dielectric constant and very weak cation solvating properties (Table II), *solvolysis in trifluoroacetic acid is much faster than in any other solvent considered in this paper*. The success of this anion solvator par excellence reemphasizes the overwhelming importance of anion solvating properties in determining rates of this type of solvolysis.

(B) *tert*-Butyl Chloride. Values of $\Delta G_{tr}^\ddagger(S_{N1})$ calculated

from titrimetric rate constants for *solvolysis* have been shown³⁹ to represent the free energies of activation for *ionization* of *tert*-butyl chloride, without complications such as ion pair return and rate determining (E2C or other) elimination,⁴⁰ in polar high dielectric solvents. This S_{N1} transition state is highly polar with about 0.8 unit of positive charge spread mainly over the nine hydrogens of $(CH_3)_3C$ and 0.8 unit of negative charge on chlorine.^{3,15} The charge separation is about 2.3 Å.¹⁵ It is important to note that much of the positive charge is spread over nine equivalent hydrogen atoms, which are hard acids, and the developing *tert*-butyl carbonium ion has considerably greater surface charge than the developing cation II of *p*-methoxyneophyl tosylate. This highly polar transition state will respond linearly to the changes in cation and anion solvating power on solvent transfer, so that eq 1, a general expression for S_{N1} solvolysis reactions, whether limiting or not, is followed.

Ferrocene-like assumptions do not apply to the solvolysis of *tert*-butyl chloride, but, as discussed, do apply to *p*-methoxyneophyl tosylate. The difference between *tert*-butyl chloride (M^0) and *p*-methoxyneophyl tosylate solvolysis is that the developing *tert*-butyl cation (M^+), like Me_3S^+ and NMe_4^+ ,^{2,3} is small enough and of sufficient surface charge to be solvated in water by the first kind of solvation mechanism,^{11,25,38} so $\Delta G_{tr}(M^+)$ does not equal $\Delta G_{tr}(M^0)$ in water or formamide, and eq 1, rather than eq 17 or 18, must be used.

The partial success of eq 17 and 18 (Table VI) in correlating rates of solvolysis of *tert*-butyl chloride suggest that $p \Delta G_{tr}(K^+)$, the cation solvating contribution to $\Delta G_{tr}^\ddagger(S_{N1})$ in eq 1, is usually negligible.

Equations 1, 17, and 18 are applied in Table VI to the solvolysis of *tert*-butyl chloride, using the anion and cation solvating parameters of Table II and observed values for $\Delta G_{tr}(t\text{-BuCl})$. A value of 0.50 was used for n and 0.65 for n' ; these fit eq 17 and 18. A value of 0.20 was chosen for p and 0.28 for p' , so as to fit the observed $\Delta G_{tr}^\ddagger(S_{N1})$ and eq 1. Values of $\Delta G_{tr}^\ddagger(S_{N1})$ observed and calculated from eq 1, 17, and 18 are in Table VI. Agreement is very satisfactory for eq 1, but as noted, deviations from eq 17 and 18 are observed.

Our value of 0.2 for p is supported by the following argument. Values (Table I) of $\Delta G_{tr}(Me_3S^+)$ and $\Delta G_{tr}(Me_4N^+)$, through eq 9 and p in Table III, suggest the approximate relationship $\Delta G_{tr}(Me_4N^+) \approx \Delta G_{tr}(Me_3S^+) \approx (0.5 \pm 0.1) \Delta G_{tr}(K^+)$. It has been suggested that Me_4N^+ , and more obviously Me_3S^+ , model Me_3C^+ in terms of its response to solvent transfer,^{2,3} so that $\Delta G_{tr}(Me_4N^+) = \Delta G_{tr}(Me_3S^+) = \Delta G_{tr}(Me_3C^+) = 0.5 \Delta G_{tr}(K^+)$ from eq 9. We have noted (n in Table VI) that the partial chloride ion in the transition state *t*-BuCl[±] seems to have half the response of a fully solvated chloride ion to solvent transfer. If partial Me_3C^+ has the same relative response as partial Cl^- to the fully solvated ion, then $0.5 \Delta G_{tr}(Me_3C^+)^\ddagger = [(0.5 \times 0.5) \pm 0.1] \Delta G_{tr}(K^+)$, so that a value of 0.2–0.3 for p in eq 1 is reasonable. Such a value makes $p \Delta G_{tr}(K^+)$ in eq 1 a small, even negligible term. Since $\Delta G_{tr}(t\text{-BuCl})$ in eq 1 also usually is small, the success of the approximate relationships eq 17 and 18, as well as eq 1, in correlating many solvolysis rates of *tert*-butyl chloride is readily explained.

The term $0.5 \Delta G_{tr}(Cl^-)$ dominates the right hand side of eq 1, even more so since $0.2 \Delta G_{tr}(K^+)$ and $\Delta G_{tr}(t\text{-BuCl})$ in eq 1 are of the same sign (Table II and VI) in most solvents, so that the deviation $0.2 \Delta G_{tr}(K^+) - \Delta G_{tr}(t\text{-BuCl})$ of eq 17 and 18 from eq 1 is even smaller than each term. The exception is for transfer to water, where $\Delta G_{tr}(t\text{-BuCl})$ is +18 kJ mol⁻¹ and $0.2 \Delta G_{tr}(K^+)$ is -2 kJ g-ion⁻¹ for transfer from acetonitrile to water, so that eq 17 differs from eq 1 by 20 kJ mol⁻¹ in its attempt to correlate $\Delta G_{tr}^\ddagger(S_{N1})$. Equation 18 is even less successful than eq 17. Likewise, eq 18 gives increasing positive deviations for methanol–water mixtures with increasing water

content, whereas excellent agreement is obtained by eq 1.

Having demonstrated the significance of eq 1 in solvolysis of *tert*-butyl chloride, we note that Abraham also showed the occasional influence of $\Delta G_{tr}(t\text{-BuCl})$ in determining rate and developed a very satisfactory linear free-energy relationship (eq 24 and 25). This effectively uses a partial ion pair, $\text{Me}_4\text{N}^+\text{Cl}^-$, as a model for the transition state $t\text{-BuCl}^\ddagger$.³ Equation 25 is valid for polar high dielectric solvents, but like eq 18, shows deviations for low dielectric solvents. Abraham comments that he finds a *poor* relationship, eq 26. This, via eq 9 with $M^+ = \text{Me}_4\text{N}^+$, is identical to our relationship eq 1, except for different sensitivities. Abraham did not in fact separate $\Delta G_{tr}(\text{Me}_4\text{N}^+) + \Delta G_{tr}(\text{Cl}^-)$ in eq 26 into individual ionic transfers, and so was forced to allocate the *same* sensitivity to anion and cation solvating properties. Thus he was unable to comment on the relative importance of anion and cation solvation in determining $\Delta G_{tr}^\ddagger(\text{S}_{N1})$. His rejection of eq 26 and adoption of eq 25 lead him to conclude that the S_{N1} transition state has a structure between reactants and ion pair, not one between ion pair and solvated, separated ions.⁴¹ This question is not answered by our analysis, despite the apparent implications of eq 1 and 23. As noted, we have more confidence in relationships based on separately determined $\Delta G_{tr}(\text{Cl}^-)$ and $\Delta G_{tr}(\text{K}^+) + \Delta G_{tr}(\text{Me}_3\text{S}^+) + \Delta G_{tr}(\text{Cl}^-)$, $\Delta G_{tr}(\text{Cs}^+) + \Delta G_{tr}(\text{Cl}^-)$,³² $\Delta G_{tr}(\text{Me}_4\text{N}^+) + \Delta G_{tr}(\text{Cl}^-)$, or $\Delta G_{tr}(\text{Me}_4\text{N}^+\text{Cl}^-)$ from solubility and conductance measurements. This is because of the advantages of potentiometry over solubility methods for determining ΔG_{tr} values of these single ions.^{22,23,25}

$$\Delta G_{tr}(t\text{-BuCl}^\ddagger) = 0.67\Delta G_{tr}(\text{Me}_4\text{N}^+\text{Cl}^-) \quad (24)$$

$$\Delta G_{tr}^\ddagger(\text{S}_{N1}) = 0.67\Delta G_{tr}(\text{Me}_4\text{N}^+\text{Cl}^-) - \Delta G_{tr}(t\text{-BuCl}) \quad (25)$$

$$\Delta G_{tr}^\ddagger(\text{S}_{N1}) \approx 0.39\Delta G_{tr}(\text{Me}_4\text{N}^+) + 0.39\Delta G_{tr}(\text{Cl}^-) - \Delta G_{tr}(t\text{-BuCl}) \quad (26)$$

Equation 18 is not adequate for correlating the effects on $\Delta G_{tr}^\ddagger(\text{S}_{N1})$ of transferring the solvolysis of *tert*-butyl chloride from high dielectric to very low dielectric solvents like ether, dioxane, *n*-heptane, acetic acid, and trifluoroacetic acid. The equations predict faster solvolyses than are observed in these low dielectric solvents and this can be explained in part by eq 1, which introduces a term allowing for the poor cation solvating properties of these solvents. Values of $\Delta G_{tr}(t\text{-BuCl})$ are still negligible (Table VI) for transfer to low dielectric solvents, so eq 1 can be written as the approximate relationship eq 27, which improves the correlation significantly for transfer to DMF, DMA, NMePy, and Me_2SO , which are strong cation solvators. The coefficients in eq 27 for $\Delta(\text{DN})$ and $\Delta(\text{AN})$ follow from p' and n' (Table III) in eq 11 and 12, respectively. However, as shown in Table II, the relationships eq 11 and 12 which lead to eq 27 are very uncertain for low dielectric solvents, and it is not profitable to use eq 27 for solvolysis rates in ether, heptane, and dioxane.

$$\Delta G_{tr}^\ddagger(\text{S}_{N1}) = 0.2\Delta G_{tr}(\text{K}^+) + 0.5\Delta G_{tr}(\text{Cl}^-) - 0.3\Delta(\text{DN}) - 0.72\Delta(\text{AN}) \quad (27)$$

In summary, eq 1, 27, 17, and 18 give decreasingly less comprehensive correlations of the rates of solvolysis of *tert*-butyl chloride in different solvents. However, even eq 17 and 18 are satisfactory for transfer through a wide range of solvents, where the combined effects of changes in cation solvation and in solvation of *t*-BuCl can be neglected.

We note the success of the reaction field method in explaining solvolysis rates of *tert*-butyl chloride in a limited number of solvents which are weak anion solvators.¹⁵ However, dipole moment, quadrupole moment, molar volume, and refractive index of the transition state and solutes, coupled with the dielectric constant of the solvent, cannot explain the

differences between rates of solvolysis of *tert*-butyl chloride in trifluoroacetic acid and nitrobenzene, trifluoroethanol and ethanol, methanol and dimethylformamide, acetonitrile and acetic acid, and Me_2SO -acetonitrile (Table VI). Anion solvating power and cation solvating power, as distinct from general electrostatic ion solvating power, must be taken into account when considering solvolysis of *tert*-butyl chloride in a wider range of solvents.⁸ Anions and cations have specific and different "chemical" interactions with solvents. No theory based on solvent dielectric constant, dipole moment, quadrupole moment, etc., can hope to be generally applicable to the detailed chemistry of ions in solution.^{2,13,25}

(C) *tert*-Butyl Bromide and *trans*-4-*tert*-Butylcyclohexyl Tosylate. The analysis for solvolysis rates of *tert*-butyl bromide, in terms of eq 1, is in Table VI. Since bromide, rather than chloride, is now the leaving group, n is only 0.35, rather than 0.5; i.e., the solvolysis is less sensitive than that of *tert*-butyl chloride to anion solvating power. We use $0.2\Delta G_{tr}(\text{K}^+)$, assuming the same sensitivity to cation solvating power for *t*-BuBr and *t*-BuCl. The deviations and the correlations in Table VI can be explained in the same way as for the solvolysis of *tert*-butyl chloride.

The analysis of rates of solvolysis of *trans*-4-*tert*-butylcyclohexyl tosylate (ROT) at 75 °C (Table VII)^{42,43} can only be semiquantitative at this time, because $\Delta G_{tr}(\text{ROT})$ is unknown and there are insufficient data points fitting eq 1 to give accurate values of n and n' . Despite these difficulties, the analysis in Table VII is worthwhile, especially because the data are for solvolysis at a secondary carbon atom. Tables V-VII show three situations. Table V analyzes data for solvolysis at a primary carbon atom, with full participation from a neighboring 4-methoxyphenyl group. There is a requirement for extensive solvation of the leaving tosylate ($n' = 0.52$). Table VI analyzes data for solvolysis at the tertiary carbon with less sensitivity to anion solvating power, and Table VII analyzes data for solvolysis of a secondary tosylate, with some neighboring hydrogen participation.⁴³ Table VII shows a partial analysis in terms of eq 1 and a full analysis in terms of eq 18, with $n' = 0.5$ for this tosylate, as determined by the "fit" for ethanol, nitromethane, acetonitrile, acetone, and acetic acid. Knowing $n'\Delta(\text{AN})$ and $\Delta G_{tr}^\ddagger(\text{S}_{N1})$ allows calculation of $p\Delta G_{tr}(\text{K}^+) - \Delta G_{tr}(\text{ROT})$, as shown in Table VII. We expect^{2,3} $\Delta G_{tr}(\text{ROT})$ for transfer through the solvents of Table VII to be no more than $\pm 2 \text{ kJ mol}^{-1}$, so the significant deviations from eq 18 of up to 14 kJ mol^{-1} for solvolysis in $\text{CF}_3\text{CO}_2\text{H}$, and ca. -8 kJ mol^{-1} for solvolysis in Me_2SO and DMF are due to a stronger sensitivity of this solvolysis to cation solvating power. As shown in Table VII, a value of $\sim 0.4\Delta G_{tr}(\text{K}^+) - 0.5\Delta(\text{AN})$ fits the observed values of $\Delta G_{tr}^\ddagger(\text{S}_{N1})$ to eq 1 with modest success. Certainly the need to take account of the cation solvating power of the solvents is apparent for solvolysis of this tosylate.

In summary, the sensitivity to cation solvating power (Table II) of the solvolysis of *p*-methoxyneophyl tosylate (0.1), *tert*-butyl chloride (0.2), and *trans*-4-*tert*-butylcyclohexyl tosylate (0.4) increases in the order of p values (eq 1) shown in parentheses. Thus eq 17 and 18 (i.e., eq 3) are very satisfactory for correlating rates of solvolysis of *p*-methoxyneophyl tosylate, are of some value for correlating solvolysis of the *tert*-butyl halides, but are likely to be of very limited value for solvolysis of secondary halides and tosylates.

The expression $\Delta G_{tr}^\ddagger = \pm n\Delta G_{tr}(\text{Cl}^-) = \mp n'\Delta(\text{AN})$ is a very useful "rule of thumb" for estimating solvent effect on rates of S_{N1} and S_{N2} reactions of the charge type shown. Care is necessary when considering reactions in structured solvents like water and formamide.

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Analytical Solution to the Curtin-Hammett/Winstein-Holness Kinetic System¹

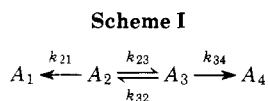
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The analytical solution is presented for the kinetic scheme involving a starting material which exists in two isomeric forms, each of which reacts via first-order or pseudo-first-order kinetics to give a different product. This kinetic scheme has been approximated by the well-known Curtin-Hammett (C-H) principle (in terms of product ratios) and by the Winstein-Holness (W-H) equation (in terms of reaction rate). The versatility of the exact solution is discussed especially with regard to the range of validity of the C-H/W-H approximations.

Conformational analysis commands a central role in the understanding of the physical properties and the chemical reactivity of molecules.² Almost 25 years ago, Curtin and Hammett,³ Winstein and Holness,⁴ and Eliel and Ro⁵ independently considered the chemical consequences of a system in which the starting material exists in two distinct equilibrating forms, each reacting to give a different product (Scheme I).⁶



Two principles dealing with this kinetic scheme were advanced. The Curtin-Hammett (C-H) principle stated that the ratio of the products formed "depends only on the relative

energy levels of the transition states by which the products are formed, provided that the activation energy for product formation is large compared to the activation energy for the interconversion of the isomeric starting materials"⁷ (eq 1).⁸ The Winstein-Holness (W-H) equation approximated the overall rate constant for total product formation as the time-independent quantity shown in eq 2.^{4,5,9}

$$\frac{A_4}{A_1} = \frac{k_{23} k_{34}}{k_{32} k_{21}} = K \frac{k_{34}}{k_{21}} \quad (1)$$

$$k_{\text{WH}} = \frac{k_{34}K + k_{21}}{K + 1} \quad (2)$$

The Winstein-Holness relationship and the Curtin-Hammett principle have been valuable approximations be-