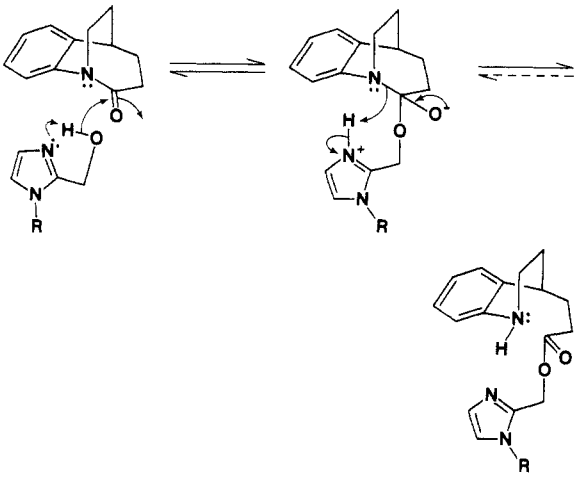
imidazole with 1 which is 60, 1.92×10^{-2}, and 9.53×10^{-4} M^{-1} s^{-1}, respectively while for pNPA the ordering is 15,[28a] 3.4×10^{-1}, and 4.5×10^{-2} M^{-1} s^{-1},[28b,c] respectively. Thus, the more sterically encumbered nucleophile, 2-methylimidazole is 50-fold less nucleophilic toward 1 than pNPA, while the smaller nucleophile OH^- is 4-fold more nucleophilic. Presumably, O attack on 1 would not be subject to as severe steric encumbrance as would N attack. On the other hand in the case of reaction of the amino alcohols with the less sterically encumbered C=O unit in pNPA, the N when neutral is inherently more nucleophilic than OH and becomes acylated.

An alternative explanation similar to that invoked by Tonellato[3m] utilizing the relative leaving group abilities from tetrahedral intermediates produced from attack on esters such as pNPA with good leaving groups or activated amides with poorer leaving groups can be advanced. Our previous studies[6,29] have shown that whereas attack of the strongly nucleophilic OH^- on 1 proceeds irreversibly, attack of a weaker nucleophile H_2O on the neutral amide or 1-H^+ proceeds reversibly. There remains a possibility that with the amino alcohols studied here, neither nucleophilic attack nor breakdown of the tetrahedral addition intermediate is entirely rate limiting. Hence in the case of nucleophiles that are also good leaving groups (i.e., imidazole), the reversal of addition could be prominent and the overall rate of reaction by that pathway slow. It may be envisioned as in eq 6 that the breakdown of the tetrahedral intermediate formed from O attack is facilitated by intramolecular general-acid catalysis by the pendant protonated



(6)

amine. While the proposal remains speculative in this case, it is interesting that the accepted mechanism of acylation of the serine group in chymotrypsin involves an analogous process.

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Registry No. 1, 102586-88-9; **2a**, 108-01-0; **2l**, 67-48-1; **3oa**, 3724-26-3; **3a** (acetate), 45815-85-8; **3b**, 693-98-1; **4a**, 17334-08-6; **4a** (acetate), 104876-20-2; **4b**, 1739-84-0; TRICENE, 5704-04-1; TRIS, 77-86-1; HEPES, 7365-45-9; BISTRIS, 6976-37-0; *p*-NPA, 830-03-5; (*N*,*N*-dimethylamino)ethyl 1,2,3,4-tetrahydroquinoline-4-propanoate, 104876-18-8; (*N*-methyl-2-imidazolyl)methyl 1,2,3,4-tetrahydroquinoline-4-propanoate, 104876-19-9.

Supplementary Material Available: Listings of anisotropic and isotropic thermal parameters (Table 1), positional parameters for hydrogen and non-hydrogen atoms (Tables 3 and 4), bond distances (Table 5), bond angles (Table 6), and observed second-order rate constants (Tables 7-9), and ORTEP view of amide 1 (9 pages); listings of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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(29) Šlebocka-Tilk, H.; Somayaji, V.; Brown, R. S., submitted for publication.

(30) **Noted Added in Proof**: After the acceptance of this manuscript, a paper appeared reporting torsional angles of a coordinated amide comparable to those reported here: Collins, T. J.; Coots, R. J.; Furutani, T. T.; Keech, J. T.; Peake, G. T.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1986**, *108*, 5333.

Linear Solvation Energy Relationships. 39. A Double-Difference Method for Estimating Electrophilic Solvent Assistance Effects in Solvolysis Reactions

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Solvent effects on solvolysis rates may be expressed by a linear solvation energy relationship that combines terms that measure solvent dipolarity/polarizability (SDP) effects, electrophilic solvent assistance (ESA), nucleophilic solvent assistance (NSA), and solvent electrostrictive effects (CAV = a cavity term). A method of double differences is presented, by which an estimate of ESA can be obtained for systems in which there is no NSA. The method requires that the rates of reaction be measured in four solvents—methanol, ethanol, trifluoroethanol, and hexafluoro-2-propanol.

During the course of the past 30 years, many investigations in physical organic chemistry have dealt with mechanisms of solvolysis reactions, and numerous schemes have been devised for sorting out the contributions of nucleophilic solvent assistance (NSA) and "solvent ionizing power" (SIP) to solvolysis reaction rates. SIP has long been recognized[1] as including contributions of solvent

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dipolarity/polarizability (SDP) and electrophilic solvent assistance (ESA), the assumption in most classical approaches to the problem being that ESA is either constant for a given leaving group or that it varies linearly with SDP.

We have recently shown that, in addition to SDP, NSA, and *variable* ESA, *tert*-butyl and 1-adamantyl halide solvolysis rates in hydroxylic solvents are also influenced by a cavity term (CAV) that includes a strong exoergic contribution from solvent electrostriction (strengthening of the hydrogen-bonded network) around the developing transition-state halide ion.[2] Accordingly, solvent effects on solvolysis rates may be described by linear solvation energy relationships that include linear combinations of terms measuring the effects of the four contributing solute–solvent interactions (eq 1).

$$\log k = (\log k)_0 + h(\mathrm{CAV}) + s(\mathrm{SDP}) + a(\mathrm{ESA}) + b(\mathrm{NSA}) \quad (1)$$

The demonstrated variability of ESA for substrates having the same leaving group[2] has interesting mechanistic implications. In particular, it is quite probable that many previous estimates of the magnitude of NSA in solvolysis of primary and secondary substrates are inflated because of the assumption that ESA is invariant. For example, a recent work with β-thioethyl derivatives gave nonlinear Raber–Harris plots (consistent with NSA in these reactions), yet other experiments clearly showed the absence of NSA.[3] The prime suspect in this apparent contradiction is the assumption of ESA invariance in the Raber–Harris method. In order to explore fully questions of this nature, we must be able to sort out contributions from the different solvent–solute interactions and measure values of the coefficients a, b, h, and s.

In attempting to separate the individual effects and estimate their magnitudes, two problems arise. First, for the substrates that can undergo HX elimination, the data sets can include results in both hydrogen bond donor (HBD) and non-HBD solvents. (In treating these data as a coherent set one must make the assumption that the solvolysis and dehydrohalogenation transition states show similar responses to solvent properties.) However, many substrates for which NSA can be dismissed from consideration because of steric impairment of backside approach (e.g., 1-adamantyl halides) cannot normally undergo elimination, and hence their reactions become quite complex in HBD solvents.[4] This means that these reactions have typically been run in limited numbers of pure solvents, typically five to eight, and it is impossible to get reliable and statistically valid estimates of the four remaining adjustable parameters ($\log k_0$, a, h, and s) from such limited data sets.

Second, for the HBD solvents commonly used in these studies, the important solvent parameters are highly correlated with one another, making it difficult to separate cleanly the various effects. Kevill and co-workers[4] have characterized as "nature's cruel trick" the fact that, for the commonly used solvents, the solvent nucleophilicities increase approximately linearly with decreasing SIP and that an effect attributed to an increase in the one property might actually be due to a decrease in the other. In a similar vein, we have recently shown[5] that, for water and the commonly used alkanol solvents, the parameters we use to measure the CAV, SDP, ESA, and NSA effects covary strongly with one another, with correlation coefficients for the pairwise correlations exceeding 0.98. Many rate studies have been done in mixed aqueous solvents with varied water content, but this does not alleviate the correlation problem. Even if one could assign values to the parameters of the mixed solvents (which is difficult to do meaningfully because of the likelihood of solvent sorting[6]), one would only have more points with the same correlation problem.

The difficulties outlined above can be illustrated by a comparison of solvent effect correlations for the solvolyses of *tert*-butyl chloride (*t*-BuCl) and 1-adamantyl chloride (1-AdCl). The specific solvent parameters that we have chosen to measure the contributions of NSA, ESA, SDP, and CAV effects to the rates are the solvatochromic parameters[7-9] β, α, and π^* and the square of the Hildebrand solubility parameter δ_H^2 (scaled by 1/100 to make it the same order of magnitude as the other parameters). The

Table I. Solvents in Which *tert*-Butyl Chloride Solvolysis/Heterolysis Rates Are Available

non-hydrogen bond donors	hydrogen bond donors
dimethylacetamide	acetone[a]
dimethylformamide	acetonitrile[a]
dioxane	1-butanol
ethyl acetate	*tert*-butyl alcohol
N-methylpyrrolidone	ethanol
tetrahydrofuran	ethylene glycol
	formamide
	hexafluoro-2-propanol
	methanol
	nitromethane[a]
	1-propanol
	2-propanol
	trifluoroethanol
	water

[a] These compounds are listed as HBD solvents because they have nonzero values of α. However their HBD acidity is so small that they do not appreciably affect the rate of reaction by ESA.

Table II. Correlation Coefficients for Pairwise Correlations of Solvent Parameters[a]

	α	β	π^*	δ_H^2
α	1.000	−0.328	0.055	0.359
	(1.000)	(−0.887)	(0.221)	(−0.101)
β		1.000	−0.315	−0.174
		(1.000)	(−0.606)	(−0.286)
π^*			1.000	0.656
			(1.000)	(0.872)
δ_H^2				1.000
				(1.000)

[a] The values in the first line of each row are for 21 point correlations, using data for the compounds listed in Table I. The second line (values in parentheses) are for 11 point correlations, using the nine alcohols listed in Table I, water, and formamide. Parameter values are given in ref 2.

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solvatochromic parameter β is a measure of hydrogen bond acceptor basicity and, following Swain's definition of "basity",[10] we have taken it to reflect the ability of the solvent to provide nucleophilic assistance to the reaction. Similarly, we use α, which measures hydrogen bond donor acidity or "acity" to reflect the ability of the solvent to provide electrophilic assistance. Solvent dipolarity/polarizability is measured by π^* to give a term that is directly related to non-ESA solvent ionizing power. Finally, we have also included the term in δ_H^2 to measure the solvent electrostriction effect. Substituting these specific parameters into eq 1 gives eq 2.

$$\log k = (\log k)_0 + h\delta_H^2/100 + s\pi^* + a\alpha + b\beta \quad (2)$$

In Table I we have assembled a list of the solvents in which the *t*-BuCl solvolysis/dehydrohalogenation rate has been measured. Table II shows the correlation coefficients for all the pairwise correlations of the solvent parameters involved in eq 2 based on (a) the set of all the solvents in Table I and (b) the 11 stronger HBD solvents (excluding acetone, acetonitrile, and nitromethane). As can be seen in Table II, the correlations of the solvent parameters for the whole solvent set are tractable, the worst case being for the correlation of δ_H^2 with π^*. The least squares fit of the *t*-BuCl rate data to these solvent parameters gives eq 3.

$$\log k = (-14.58 \pm 0.29) + (0.48 \pm 0.07)\delta_H^2/100 + (5.09 \pm 0.38)\pi^* + (4.17 \pm 0.12)\alpha + (0.71 \pm 0.22)\beta \quad (3)$$

$$n = 21;\ r = 0.9973;\ \text{sd} = 0.24$$

When only the HBD solvents are considered, the correlation between α and β is so high as to make any correlation involving these terms highly suspect. Moreover, the correlation of π^* with δ_H^2 is nearly as strong as that between α and β. Thus, for compounds like 1-AdCl that have been studied in HBD solvents, the available data are from the set which suffers from the worst correlations among the solvent parameters.

It is also important to note that, even in those cases in which rates can be determined in the requisite 20 or so solvents, it is still a formidable experimental undertaking to obtain accurate rates in all these cases. Consequently, it would be highly significant if a method for determining even one of the coefficients in eq 2 could be developed that requires a substantially smaller number of rates. In this work we present such a method, by which the value of a may be estimated from the rates of solvolysis in just four solvents: methanol (MeOH), ethanol (EtOH), 2,2,2-trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP).

Results and Discussion

If compounds for which NSA is unimportant (such as 1-AdCl) are considered, we can use rates in only four solvents (MeOH, EtOH, TFE, and HFIP) to arrive at a reasonably reliable estimate of the ESA effect through a procedure that we refer to as the method of double differences. This method takes advantage of the fact that differences in π^* and $\delta_H^2/100$ values are similar between EtOH and MeOH and between TFE and HFIP but that differences in α values are quite dissimilar between these pairs.

We define, in eq 4–8, two difference terms, Δ_1P and Δ_2P, and a double-difference term, $\Delta\Delta P$, where P is a solvent parameter or log (rate constant). It is seen that the $\Delta\Delta P$ values are small for $\delta_H^2/100$ and π^*, somewhat larger for β,[11] and largest for α. These double differences in the solvent parameters should be reflected in the corresponding double differences in log k, and an equation relating $\Delta\Delta$ log k to the $\Delta\Delta P$ terms can be derived from eq 2.

$$\Delta_1P = P_{HFIP} - P_{TFE} \quad (4a)$$

$$\Delta_2P = P_{EtOH} - P_{MeOH} \quad (4b)$$

$$\Delta\Delta P = \Delta_1P - \Delta_2P \quad (4c)$$

$$\Delta_1\delta_H^2/100 = 0.893 - 1.371 = -0.478 \quad (5a)$$

$$\Delta_2\delta_H^2/100 = 1.621 - 2.052 = -0.431 \quad (5b)$$

$$\Delta\Delta\delta_H^2 = -0.047 \quad (5c)$$

$$\Delta_1\pi^* = 0.65 - 0.73 = -0.08 \quad (6a)$$

$$\Delta_2\pi^* = 0.54 - 0.60 = -0.06 \quad (6b)$$

$$\Delta\Delta\pi^* = -0.02 \quad (6c)$$

$$\Delta_1\beta = 0.00 - 0.00 = 0.00 \quad (7a)$$

$$\Delta_2\beta = 0.77 - 0.62 = 0.15 \quad (7b)$$

$$\Delta\Delta\beta = -0.15 \quad (7c)$$

$$\Delta_1\alpha = 1.96 - 1.51 = 0.45 \quad (8a)$$

$$\Delta_2\alpha = 0.83 - 0.93 = -0.10 \quad (8b)$$

$$\Delta\Delta\alpha = 0.55 \quad (8c)$$

$$\Delta\Delta \log k = a(0.55) + b(-0.15) + s(-0.02) + h(-0.047) \quad (9)$$

For 1-AdCl and other reactants *for which there is no NSA*, the second term drops out ($b = 0$). If s and h are assumed to be of such magnitudes that $-0.02s$ and $-0.047h$ are small compared to $\Delta\Delta$ log k, then a, which reflects the sensitivity of the solvolysis rate to ESA, can be estimated by eq 10. In the case of *t*-BuCl, the $-0.02s$ and $-0.047h$

$$a \simeq (\Delta\Delta \log k)/0.55 \quad (10)$$

terms total about −0.10 log unit, primarily due to the former term.

Using eq 10, we estimate a to be 6.5 for 1-AdCl solvolysis at 25 °C (see Table III), which means that contributions of ESA to log rate constants amount to about 6.5α, corresponding to 12.7 log unit for HFIP, 9.8 for TFE, 7.6 for H_2O, and 6.0 for MeOH. By means of a much more convoluted calculation and on the assumption that the 1-AdCl rate was modeled by *t*-BuCl insofar as the SDP and CAV terms are concerned, we earlier[2] arrived at a similar a value of 6.46 for 1-AdCl solvolysis. If the b value of 0.71 from eq 3 is used to correct $\Delta\Delta$ log k (*t*-BuCl) for the effect of NSA, one calculates a (eq 10) for *t*-BuCl to be 4.29, which agrees reasonably well with the 21 solvent correlation value of 4.17. In a similar vein, the a (eq 10) estimate of 3.20 for *tert*-butyl bromide (for which NSA effects have been shown not to be statistically significant)[2] compares with a value of 3.16 in the 21 solvent correlation equation.

In Table III we have assembled estimates of a for two *tert*-butyl, four 1-adamantyl, three 2-adamantyl, and two norbornyl derivatives. The ordering of the a values is much as expected. Thus the I < Br < Cl order for the 1-adamantyl derivatives is similar to the ordering of the a values in equations of form similar to eq 2, but excluding

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(11) There are indications that TFE may exhibit some very slight HBA basicity ($\beta = 0.05$), but it is probably too low to allow effective complexing with the carbonium ion. Insofar as the cases dealt with herein do not involve NSA, the nonzero value makes no difference in the conclusions.

Table III. Calculation of *a* Values by the Method of Double Differences[a]

no.	reactant	log $k^{b,c}$ HFIP	log $k^{b,c}$ TFE	Δ_1 log k	log k^b EtOH	log k^b MeOH	Δ_2 log k	$\Delta\Delta$ log k	a	data ref
1	*tert*-butyl chloride	−2.70	−3.98	1.28	−7.07	−6.10	−0.97	2.25	4.09	2
1a	*tert*-butyl chloride-0.71β[d]	−2.70	−3.98	1.28	−7.62	−6.54	−1.08	2.36	4.29	2
2	*tert*-butyl bromide[e]	−1.75	−2.62	0.87	−5.35	−4.46	−0.89	1.76	3.20	2
3	1-adamantyl chloride	−3.01	−5.27	2.26	−10.60	−9.30	−1.30	3.56	6.47	18
4	1-adamantyl bromide	−2.04	−4.02	1.98	−9.00	−7.68	−1.32	3.30	6.00	18
5	1-adamantyl iodide	−2.40	−4.02	1.62	−8.43	−7.08	−1.35	2.97	5.40	19
6	1-adamantyldimethylsulfonium triflate[f]	−6.52	−6.56[g]	0.04	−1.12	−1.00	−0.12	0.16	0.29	21
7	2-adamantyl perchlorate			2.15			−1.00	3.15	5.73	21
8	2-adamantyl tosylate	−4.01	−5.79	1.78	−9.37	−8.54	−0.83	2.61	4.74	22
9	2-adamantyl triflate			0.85			−0.52	1.37	2.49	21
10	2-*exo*-norbornyl tosylate	−0.77	−2.36	1.59	−5.33	−4.46	−0.87	2.46	4.47	23
11	2-*endo*-norbornyl tosylate	−3.96	−5.30	1.34	−7.82	−6.99	−0.83	2.17	3.94	23

[a] Values of a were calculated with eq 10. [b] log k is given for rates at 25 °C, except as noted. [c] Rates for TFE and HFIP were for 97% TFE or HFIP (3% H_2O). [d] The quantity -0.71β corrects log k for nucleophilic assistance. See eq 3. [e] It has been shown that the nucleophilic assistance term in *t*-BuBr solvolysis is not statistically significant. See ref 2. [f] Rates determined at 49.7 °C. [g] Value estimated for rate in 100% TFE.

the $b\beta$ term, for free energies of transfer between solvents of the tetramethyl and tetraethylammonium halide dissociated ions and ion pairs.[12] A similar ordering has also been observed for free energies of hydration of the gas-phase halide ions.[13] Presumably the higher a values result from a more concentrated charge for the poorer leaving group and thus stronger hydrogen bonding. A more dramatic trend in a values is observed for the 2-adamantyl perchlorate, tosylate, and triflate esters, where there is a larger difference in leaving group ability. This may well be due to the weaker hydrogen bonding for the highly dispersed charge of the better leaving group, although transition-state variation (early versus late) may also be a factor. The smallest a value in Table III is for 1-adamantyldimethylsulfonium triflate. It is expected that the value of a should be 0 (i.e., no ESA) for the positively charged reactant, and indeed the value determined for a is very small (0.29). The deviation of a from 0 may be attributable partly to the necessity of using an estimated value for the rate in TFE and partly to the inherent imprecision of assuming that all other contributing factors are negligible.

We have already alluded to the higher a values for 1-AdCl and 1-AdBr compared to *t*-BuCl and *t*-BuBr. These results, which show that ESA effects are not necessarily identical where the leaving group is the same, have been rationalized[2] on the basis of the transition state leading to the 1-adamantyl cation being more advanced than that leading to the *tert*-butyl cation. In the more advanced transition state there will be more negative charge on the developing halide anion. Alternatively, the *tert*-butyl transition state is accessible from the backside and thus may receive some nucleophilic solvation, whereas 1-Ad heterolysis cannot receive such assistance. Thus there may be more demand for ESA in 1-Ad solvolysis.

The greater a value for 1-AdCl than for *t*-BuCl means that a log–log plot of rates for these two compounds in a series of solvents will not be linear. Previous studies[14,15] have shown that the plots indeed are nonlinear with *t*-BuCl being too slow in weakly nucleophilic solvents such as TFE, TFA, and HFIP. These deviations were previously interpreted as being the result of NSA in *t*-BuCl solvolysis. However, the present results emphasize that a portion of this deviation also comes from ESA by these same solvents, which in addition to being weakly nucleophilic are also strongly electrophilic. This same limitation applies to many other applications of these plots according to the Raber–Harris method.[16]

Finally we emphasize that eq 10 and the method of double differences is meant to be applied to substrates for which NSA is absent. As can be seen from eq 9, applying eq 10 to a substrate for which NSA occurs will give an a value that is too low. For example, in the case of *t*-BuCl (Table III) ignoring the finite value of b (0.71) and applying eq 10 gives an a value of 4.09, whereas the corrected value is the larger 4.29. Possibly, the slightly lower a value for *endo*-norbornyl tosylate as compared to *exo*-norbornyl tosylate is the result of weak NSA for the endo isomer.[17] However, for compounds in which NSA occurs, or is suspected to occur, shortcuts will not suffice, and it is necessary to solve eq 2 completely by determining rates in a much larger series of solvents.

Conclusion

The method of double differences provides a means of estimating ESA in solvolysis reactions that involve no NSA. Its main virtue is its simplicity, requiring as it does that the rates be measured in only four solvents. As long as its limitations are recognized (the assumption that CAV and SDP do not contribute appreciably to $\Delta\Delta$ log k; the combination of all errors and uncertainties in the rate determinations being lumped into the estimate of a), it can provide a useful tool to physical organic chemists in the analysis of solvent effects on reaction rates.

Registry No. MeOH, 67-56-1; EtOH, 64-17-5; CF_3CH_2OH, 75-89-8; $CF_3CH(OH)CF_3$, 920-66-1.

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