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Correlation of solvolysis rates with intrinsic medium properties

Sonya Johl
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**CORRELATION OF SOLVOLYSIS RATES
WITH INTRINSIC MEDIUM PROPERTIES**

A Thesis

Presented to

The Faculty of the Department of Chemistry

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Arts

By

Sonya Johl

May 1996

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ABSTRACT

CORRELATION OF SOLVOLYSIS RATES WITH INTRINSIC MEDIUM
PROPERTIES

by Sonya Johl

Solvolytic rate data of adamantyl systems are evaluated in terms of medium composition and the results are compared to those derived from the traditional Grunwald-Winstein approach. Generally, plots of log rate versus solvent ionizing power result in separate lines (dispersion) for each binary solvent pair. The rate data for various substrates in different solvents are assessed to account for dispersion.

An objective of this project is to evaluate the validity of using dispersion as a mechanistic probe for assessing nucleophilic solvent assistance. Another goal is to determine whether dispersion can be accounted for by intrinsic properties of the medium. Results of the correlations of solvolyses rates with a molecular volume function of the medium are presented and the mechanistic implications discussed.

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INTRODUCTION

Solvolysis Reactions

Nucleophilic substitution reactions may be represented by the generalized displacement reaction in which a bond between two atoms is replaced by a bond between one of these atoms and a third.¹ A nucleophilic substitution reaction in which the solvent participates both as the nucleophile, as well as serving as the reaction medium is termed a solvolysis reaction. In a solvolysis reaction a solvent molecule appears as a part of the product. A solvolysis reaction can be represented as follows:

where R can be any substrate in which the central atom is a saturated (tetrahedral) carbon and X is the leaving group which usually departs as an anion (the conjugate base of a moderate to strong acid), or as a neutral molecule. An example is the solvolysis of *t*-butyl chloride (*t*-BuCl) in ethanol producing *t*-butyl ethyl ether.

Mechanistic Classifications of Nucleophilic Substitutions

Despite the fact that nucleophilic substitution reactions have been of great interest to physical organic chemists for many decades, the underlying

mechanistic pathways for these reactions are not fully understood. As a result, various mechanistic schemes have been proposed to describe the course of these reactions.

In early 1930's Hughes and Ingold made the first attempt to determine the mechanism of nucleophilic substitution reactions.^{2,3,4} They introduced a classification system in terms of two fundamental mechanisms which now form one of the cornerstones of physical organic chemistry. These mechanisms were termed S_N1 (substitution nucleophilic unimolecular) and S_N2 (substitution nucleophilic bimolecular).

The S_N2 pathway is a single step process in which the transition state contains both nucleophile and substrate. In this mechanism, a nucleophile approaches the reacting carbon atom from the side opposite to where the leaving group is attached and a bond begins to form between the electron donating nucleophile and the carbon, while the carbon-leaving group bond is breaking (equation 2).⁵

The S_N1 reaction consists of a two step process where the leaving group departs, with its bonding electron pair, in the rate-determining step

(equation 3) followed by rapid combination of the carbocation intermediate with the nucleophile (equation 4). Thus, the rate of these reactions depends only upon the substrate concentration. The slow (rate-determining) ionization (equation 3) presumably leads to a freely solvated cationic species.

In 1951, Winstein, Grunwald and Jones⁶ described the transition state of nucleophilic substitution in terms of canonical structures I, II and III.

Structures I and III represent the situation where there is no covalent interaction between the substrate and nucleophile. Structure II gains significance when covalent interaction is involved in the rate-determining step. It was proposed that nucleophilic substitutions can be classified into two categories, based on the kind of solvent interaction with the reacting carbon in the transition state:⁶ a) Limiting (Lim), where there

is no covalent interaction involved, and b) Nucleophilic (N), where covalent character exists.

The most commonly accepted mechanistic framework for a solvolysis reaction is built on the Winstein Ion Pair Scheme (Scheme 1).¹⁴

Scheme 1

According to the above mechanism a substrate (R-X) with leaving group X undergoes bond-breakage to form an intimate ion-pair intermediate $[\text{R}^+ \text{ X}^-]$, presumably as the rate-determining step. The intimate ion-pair is enclosed in a solvent cage and can dissociate to form an external ion-pair or solvent separated ion-pair $\text{R}^+ \parallel \text{X}^-$ (a cation and an anion insulated by one or

more solvent molecules). The external ion-pair can further dissociate to form freely solvated ions which do not interact with each other.

Within the ion pair scheme any of the ionized species can return to the substrate. The return of the intimate ion-pair to substrate RX is termed internal return. Return from a solvent separated ion-pair or from free ions are termed external ion-pair return and external ion return respectively.

A solvent nucleophile can react at any step in the Winstein ion pair scheme to produce the final product. If the nucleophile attacks the substrate RX in the first step of the scheme, the reaction is considered to follow an S_N2 mechanism. If the nucleophile attacks a solvent separated ion-pair or a freely solvated ion, and R-X bond cleavage actually is rate-determining, then the reaction is considered to follow an S_N1 mechanism. The case where solvent reacts with an intimate ion pair is more complex (see ahead).

The study of the mechanistic relationships between variations in substrate structure and medium composition in solvolysis reactions has been a major objective in physical organic chemistry for years. While the Winstein Ion Pair Scheme is a useful mechanistic model to discuss solvolysis reactions, it is not adequate to account for the role of the solvent in these reactions.

Harris and coworkers stated that "Nucleophilic solvent assistance can be defined as electron donation from solvent to the developing positive dipole of a reacting C-X bond, and electrophilic solvent assistance can be defined as

electron acceptance by the solvent from the leaving group.”⁷ In other words, displacement of the leaving group by solvent acting as a nucleophile signifies nucleophilic solvent assistance.¹³

Bentley and Schleyer introduced the concept of a S_N2 - S_N1 spectrum of reaction mechanisms, which involve varying amounts of nucleophilic solvent assistance.^{8,9,10,11} In order to understand the significance of nucleophilic solvent assistance, a variety of substrates were studied by observing the effects of solvent variation on solvolysis rates. The magnitude of nucleophilic solvent assistance increases from solvolyses of 2-adamantyl tosylate (**2-AdOTs**) which solvolyzes without nucleophilic solvent assistance (S_N1) to

2-AdOTs

methyl tosylate (CH_3OTs) which solvolyzes by a S_N2 pathway.⁸ A nucleophilically solvated intimate ion pair intermediate can be represented by the three resonance forms:

A similar pentacoordinate intermediate has been proposed by Doering and Zeiss¹² and Streitwieser.¹

For a solvolysis reaction in which there is evidence for both an intermediate and nucleophilic solvent assistance, Bentley and Schleyer⁸ suggested that the mechanism be called S_N2 (intermediate).⁸ The S_N2 (intermediate) is an alternative mechanism for bimolecular nucleophilic substitution and it could be called "S_N2". However, it was pointed out⁸ that since the mechanism of a direct displacement by a nucleophile in an aprotic solvent has been well established, the term "S_N2" or "classical S_N2" should continue to indicate displacement on covalent substrate leading directly to product. Accordingly, the S_N2 (intermediate) mechanism is used when there is evidence for the existence of both a reaction intermediate and nucleophilic solvent assistance in a particular reaction. This suggests that a five-coordinate species, usually regarded as a transition state, may in some cases be a nucleophilically solvated ion pair intermediate.⁹

Correlation of Solvolysis Rates

Grunwald-Winstein Equation

In 1948, Grunwald and Winstein¹⁵ introduced a linear free energy relationship (equation 5) in order to correlate specific rates of solvolysis with an empirical parameter, the solvent ionizing power (Y).

$$\log (k/k_0) = mY \quad (5)$$

Y is defined as the "ability of the medium to solvate ions and thus facilitate their separation."²² The parameter m is a measure of the sensitivity of a substrate to changes in solvent ionizing power. To determine solvent Y values, **t-BuCl**, which was assumed to solvolyze without nucleophilic solvent assistance (i.e., S_N1), was chosen as the model compound with an assigned m value of unity, and 80% (v/v) ethanol-water was selected as the standard solvent. Thus, in equation 5, k is the specific rate of solvolysis for a substrate in any solvent, and k₀ is its corresponding rate in 80% aqueous ethanol. Y values for a variety of solvents were calculated from available **t-BuCl** data. Early studies showed that plots of log k versus Y for a number of other compounds were linear with varying slopes (m). Thus, correlations of solvolytic data via equation 5 were employed as a mechanistic probe wherein

those substrates having m values near unity were believed to follow an S_N1 pathway. This general aspect of Grunwald-Winstein has become widely accepted as a mechanistic probe.

Fainberg and Winstein determined Y values for an expanded range of solvent compositions.¹⁶ From studies of various compounds^{17,18,19} such as α -phenylethyl and neophyl chlorides and bromides, they observed that plots of $\log k$ vs. Y showed a strong tendency for the dispersion of the data into separate lines, one for each binary solvent. Furthermore, the specific rates of solvolysis in acetic and formic acid were found to be lower than in aqueous ethanol mixtures of similar ionizing power.⁶

In 1951, Winstein, Grunwald and Jones⁶ introduced a more rigorous treatment of the general problem of the solvent dependence of solvolysis rates. Accordingly, solvolysis rates are discussed in terms of two relevant solvent properties, ionizing power (Y) and nucleophilic character (N). The term solvent nucleophilicity was defined as "the ability of the solvent acting as nucleophile to displace the leaving group."²² The differential equation (equation 6) was presented, where the partial derivatives, $\partial \log k / \partial Y$ and $\partial \log k / \partial N$ were introduced as measures of the contributions of solvation and covalent bond formation to carbon respectively.⁶

$$d \log k = (\partial \log k / \partial Y)_N dY + (\partial \log k / \partial N)_Y dN \quad (6)$$

In binary solvent systems such as water-ethanol, where the components are comparably nucleophilic but differ greatly in ionizing power, the $(\partial \log k / \partial Y)_N$ term signifies the m value. Winstein, Grunwald and Jones also introduced equation 7, an integrated form of equation 6, for the correlation of solvolysis rates in terms of both ionizing power and nucleophilicity, even though N values were not explicitly determined.

$$\log (k/k_0) = mY + lN \quad (7)$$

where k = solvolysis rate constant of a substrate in a solvent of interest.
 k_0 = solvolysis rate constant of a substrate in 80% aqueous EtOH.
 Y = solvent ionizing power.
 m = sensitivity of a substrate to changes in solvent ionizing power.
 N = solvent nucleophilicity.
 l = sensitivity of a substrate to changes in solvent nucleophilicity.

Equation 6 leads to the integrated form (equation 7) if the partial derivatives are considered as the constants l and m .²⁰ The integrated form reduces to equation 5 when the lN term is negligible, i.e., when $(\partial \log k / \partial N)_Y = 0$ or is constant ($\partial N \neq 0$).

Peterson and Waller studied relative solvent nucleophilicity toward cyclic halonium ions by measuring rate constants for the reaction of

tetramethylenehalonium ions with various carboxylic acids in sulfur dioxide, in an effort to overcome the problem of variable influence upon the leaving group.²¹ They found that acetic and formic acids are almost equally reactive toward halonium ions in sulfur dioxide solvent. Since the reaction is considered to be almost independent of the ionizing power of the acids, acetic and formic acids appear to have similar nucleophilicities.

As stated by Kevill and Lin, "the nucleophilicities of acetic and formic acids relative to water and the relative nucleophilicities of the components of ethanol-water mixtures are solvent dependent and relative nucleophilicities measured at low concentration in a constant solvent are probably not a reliable measure of true solvent nucleophilicities."²³

Bentley, Schadt and Schleyer defined a solvent nucleophilicity scale (N) from CH_3OTs rate data (equation 8),^{9,24} where k is the solvolysis

$$N = \log (k/k_0)_{\text{CH}_3\text{OTs}} - 0.3Y \quad (8)$$

rate constant of CH_3OTs in a solvent of ionizing power Y, and k_0 is the rate constant for solvolysis in 80% ethanol. The sensitivity of the substrate to solvent nucleophilicity (l) is defined as unity for methyl tosylate. The m value of 0.3 in equation 8 was estimated for CH_3OTs using equation 5. Kevill and Lin stated that the chosen value of m (0.3) was based on a

doubtful assumption.²³ As a result, any uncertainty arising from the mY term will contribute to the corresponding uncertainty in the scale of solvent nucleophilicities. An m value of 0.55 was estimated for triethyloxonium ion solvolysis.²⁵ The m value was found to be 0.4 in the case of ethyl tosylate solvolysis.⁹

Because **t-BuCl** was suspected to solvolyze with nucleophilic solvent assistance, **2-AdOTs** was chosen as the standard substrate. The choice of **2-AdOTs** as the model compound was based on the assumption that it solvolyzes without detectable nucleophilic solvent assistance or significant internal return. Paradisi and Bunnett²⁶ subsequently found that the rate of ¹⁸O equilibration during the solvolysis of 2-adamantyl benzenesulfonate was faster than the rate of benzenesulfonic acid production. This observation suggests that internal return does occur in such a secondary system, and that carbon-oxygen bond cleavage is not rate determining. They called for a reevaluation of the use of solvent ionizing power as a mechanistic probe. Nevertheless, new Y_x scales based on the solvolyses of 1-adamantyl substrates (**1-Ad-X**) have proliferated over the past decade.

1-AdX

Alternative Approaches

In addition to the relationships discussed above, several others were introduced to correlate solvolytic rates. In 1955, Swain, Mosely and Bown²⁷ proposed a four-parameter equation to correlate the solvolysis rates of a wide range of compounds based on a single set of parameters. As a result, equation 9 was introduced where k is the rate constant for any substrate, k_0

$$\log(k/k_0) = c_1d_1 + c_2d_2 \quad (9)$$

is the rate constant in 80% ethanol (standard solvent), c_1 and c_2 are constants which depend on the compound undergoing solvolysis, and d_1 and d_2 are constants which depend only on the solvent.²⁸ The values of d_1 and d_2 were obtained through an iterative computer-procedure wherein the following four arbitrary conditions were chosen: $c_1 = 3.00c_2$ for methyl bromide; $c_1 = c_2 = 1.00$ for *t*-BuCl; $3.00c_1 = c_2$ for (Ph)₃CF; $d_1 = d_2 = 0.00$ for 80% ethanol.

Limitations of the Swain Treatment

The Swain treatment leads to fundamental difficulties regarding the reaction mechanism since the initial c_1 and c_2 values (characteristic of the reactivity of the compound) are chosen arbitrarily.²⁰ In addition, this treatment makes no allowance for either ion pair return or leaving group

specificity.¹⁹ Consequently, Winstein, Fainberg and Grunwald described the success of this treatment as "illusory".²⁰ Swain also pointed out that some of the c_1 , c_2 , d_1 and d_2 values are surprising.²⁸ For example, increasing sensitivity to solvent nucleophilicity as reflected in increasing c_1 values is in the order of ethyl bromide (0.80) < isopropyl bromide (0.90) < t-butyl bromide (1.00). The decrease in c_1/c_2 ratio is primarily due to larger increase in c_2 .

Bentley, Schadt and Schleyer noted that the substrate factors c_1 and c_2 are of little mechanistic significance in spite of the satisfactory correlation achieved for a wide range of substrates and solvents.⁹ Peterson and Waller also stated that the results originating from the assumption regarding standard parameters were not fully understood.²¹ They pointed out that by using the alternative assumption $c_1 = 0.00$ and $c_2 = 1.00$, it can be shown that $d_1 + d_2$ should correspond to Y values. Swain used the expression $d_1 - d_2$ as a measure of solvent reactivity, which was characteristic of solvent nucleophilicity.

According to Streitwieser¹, in many cases the c_2 values in aqueous alcohol mixtures are closer to m values of the mY correlation. Apparently the interpretation of $c_1 = 0$ for t-BuCl leads to the result that methyl bromide is less sensitive to solvent nucleophilicity than the tertiary halide, which is absolutely contradictory. Another startling discrepancy is that the Swain treatment leads to the result that 1-bromobicyclo[2.2.2]octane (structurally

protected from attack at the rear) is more sensitive to backside attack than methyl bromide! Streitwieser concluded that c_1 values are completely empirical parameters and do not reflect sensitivity to solvent nucleophilicity. Streitwieser wrote, "Unfortunately, because of the conventions adopted in setting up the c_1 values, these have no theoretical significance."

A more promising starting point would include the definition $c_2 = 0.00$ for *t*-BuCl, which would change all the values of the treatment, especially the d_2 values which would be identical to the Y values.

The dubious success of the statistical four-parameter equation is due to the contributions of four adjustable parameters which are of limited utility in predicting other solvolysis rates or making mechanistic interpretations.³⁰ The treatment also provides little assistance with regard to dispersion.²⁰ For example, c_1 (1.24) and c_2 (1.25) are essentially equal for benzhydryl chloride. In Swain's treatment, $c_1 = c_2 = 1.00$ for *t*-BuCl. Therefore, using the average value of $c_1 = c_2 = 1.245$, the benzhydryl chloride rates are correlated by equation (10), and a plot of $\log k$ versus Y should give a single straight line

$$\log k = \log k_0 + 1.245 Y \quad (10)$$

for all solvent mixtures. Apparently, the observed dispersion is not anticipated.

Winstein, Fainberg and Grunwald ²⁰ support the mY treatment as the most suitable for fitting data over a narrow range of compounds and solvents. They suggest that Swain's treatment is helpful for obtaining fairly rough estimates of rate constants over a rather wide range of compounds and solvents.

Swain, Dittmer and Kaiser introduced a special two-parameter equation (equation 11) as an alternative to the four-parameter equation.²⁹

$$\log(k/k_0)_A - \log(k/k_0)_{A_0} = \mathbf{a} \mathbf{b} \quad (11)$$

As defined by Swain and co-workers, "k is the rate constant for any substrate (A) or standard compound methyl bromide (A₀) in any solvent, k₀ is the corresponding rate constant in 80% ethanol at the same temperature, **a** is a constant depending on only the chloride or bromide and **b** is a constant depending on only the solvent." The arbitrary conditions chosen were: **a** = 0.00 for methyl bromide, **a** = 1.00 for *t*-BuCl, and **b** = 0.00 for 80% ethanol.

The values of **a** and **b** were obtained by using the method of least squares in a simple iterative procedure.²⁹ Bentley and Schleyer stated that the constant **b** signifies the extent to which a solvent favors an S_N1 reaction more than does the reference solvent.³⁰ It is also related to solvation properties such as acidity and dielectric constant.

The parameter **a** determines the extent to which the solvolysis of a substrate resembles that of *t*-BuCl or methyl bromide. In other words, the factor **a** indicates the ability of the substrate to undergo heterolysis without nucleophilic solvent assistance. The precision of the correlations was found to be encouraging. Apparently the **a** values which are mechanistically significant, increasing in the order methyl bromide (0.00, defined), ethyl bromide (0.15), *n*-butyl bromide (0.18), *i*-propyl bromide (0.42) and *t*-BuCl (1.00, defined). Schadt, Bentley and Schleyer described two parameter treatment as satisfactory, but it has received little further attention.⁹

Bentley, Schadt and Schleyer introduced a three-parameter equation (equation 12) based on two standard substrates,^{9,24} 2-AdOTs as limiting (S_N1) and CH₃OTs as S_N2, where (k/k₀) is the rate of solvolysis of a substrate

$$\log(k/k_0)_{\text{ROT}_s} = (1-Q)\log(k/k_0)_{\text{CH}_3\text{OT}_s} + Q\log(k/k_0)_{2\text{-AdOT}_s} \quad (12)$$

in a given solvent, relative to 80% ethanol. Q is defined as "an adjustable blending parameter" which reflects the extent to which any substrate of interest approaches either model compound i.e. methyl (Q = 0) or 2-adamantyl (Q = 1) in solvolytic behavior.¹⁰

A further refinement of the above equation yields the Q' scale (equation 13) involving substrates **2-AdOTs** and 2-propyl tosylate.¹⁰ Q' values vary significantly suggesting a spectrum of reaction mechanisms

$$\log(k/k_0)_{\text{ROT}s} = (1-Q')\log(k/k_0)_{\text{2-PrOT}s} + Q'\log(k/k_0)_{\text{2-AdOT}s} \quad (13)$$

involving varying degrees of nucleophilic solvent assistance rather than distinct S_N1 and S_N2 processes.^{9,10}

In 1992, Kevill and Kyong proposed multiple pathways in the solvolysis of 1-adamantyl fluoroformate.³¹ The study was an extension of the solvolysis-decomposition of 1-adamantyl chloroformate.³² 1-Adamantyl chloroformate provided evidence for attack at acyl carbon only in ethanol. The only products detected were 1-adamantyl chloride from decomposition and 1-adamantanol and/or 1-adamantyl alkyl ether from a solvolysis process which was accompanied by a loss of carbon-dioxide. This pathway was defined as the solvolysis-decomposition pathway. This is also an important pathway in the solvolysis of 1-admantyl fluoroformate.

The reaction proceeded by the formation of an ion-pair $1\text{-Ad}^+\text{Cl}^-$, either through loss of carbon dioxide by a concerted process, or by a very unstable $(1\text{-AdOCO})^+\text{Cl}^-$ ion pair. The carbon-halogen bond is broken in the rate-determining step regardless of the pathway (concerted or stepwise).

The reactions of 1-adamantyl chloroformate follow only a solvolysis-decomposition pathway, while the that of 1-adamantyl fluoroformate has two major reaction pathways: i) parallel solvolysis-decomposition, and ii) bimolecular attack by the solvent at the acyl carbon.

The adamantyl fluoroformate proceeds through a solvolysis decomposition pathway about $10^4\text{-}10^5$ times slower than adamantyl chloroformate which suggests that the carbon-halogen bond breaks in the transition state rather than the rate-determining ionization to 1-adamantyl haloformate ion pair.³¹

Dispersion

Grunwald and Winstein¹⁵ reported solvolysis rates for a variety of compounds including *t*-butyl bromide, α -methylallyl chloride, α -methylneopentyl *p*-bromobenzenesulfonate, neopentyl bromide, *n*-butyl bromide and *t*-BuCl in water, ethanol-water, methanol-water and acetone-water media. They observed linear behavior when $\log k$ values for any one of the compounds were plotted against those of another in a given solvent

system. However, Fainberg and Winstein found that the data for each solvent pair gave a separate line when the $\log k$ values at 25°C for α -phenylethyl chloride were plotted vs. Y .^{17,18} Neophyl chloride and neophyl bromide solvolysis rates also exhibited the same behavior in plots of $\log k$ vs. Y .¹⁹ The phenomenon of observing separate lines in mY plots of a substrate in several binary solvent mixtures is defined as dispersion. Similar cases of dispersion have been observed in the solvolysis of a wide variety of compounds.²⁰ Hence, dispersion in mY plots is regarded as a general phenomenon. Bentley and Schleyer stated that, "the dispersion between the two lines is conveniently discussed in terms of the rate ratios in two solvents having the same values of Y ."⁸ This technique has been used extensively to evaluate the extent of nucleophilic solvent assistance.

In 1994, Kevill and co-workers introduced an approach for a quantitative treatment of dispersion by the addition of a hI term to the Grunwald-Winstein two-term (equation 5) or three-term (equation 7) equations⁵³ as shown in equations 14 and 15 respectively, where k is the

$$\log(k/k_0) = mY + hI \quad (14)$$

$$\log(k/k_0) = mY + lN + hI \quad (15)$$

specific solvolysis rate of the substrate under investigation (*p*-methoxybenzyl)dimethylsulfonium ion at 50 °C, k_0 is its solvolysis rate in 80% ethanol, h is the sensitivity of the rates to variations in aromatic ring parameter I , and m , Y , l and N are defined as in the earlier equations,. The parameter I is defined in equation 16, where Y^+ values indicate $\log(k/k_0)$ for

$$I = \log(k/k_0) - 1.3Y^+ \quad (16)$$

1-adamantyldimethylsulfonium ion solvolysis at 70.4 °C, and m (determined to be 1.3) is the sensitivity rates to variations in Y^+ .

Solvolysis rates of two different substrates [(*p*-methoxybenzyl)dimethylsulfonium ion and 1-adamantyldimethylsulfonium ion] were used to develop an aromatic ring parameter scale (I). Correlations are reported for different substrates [(*p*-methoxybenzyl)dimethylsulfonium ion, 2-chloro-2-phenyladamantane, α -(*t*-butyl)-benzyl tosylate, α -(*t*-butyl)- α -methylbenzyl chloride, *p*-methoxybenzyl chloride and benzhydryl chloride] using equations 14 and 16. In both cases, dispersion in the Grunwald-Winstein plots was eliminated.⁵³

A Diffusional Solvolysis Mechanism

Despite the multitude of studies devoted to the solvolytic process over the past 50 years, there remains considerable uncertainty about the detailed mechanism of these reactions, and the exact role played by the solvent. The definition of solvent ionizing power originally was predicated upon rate-determining ionization-dissociation of *t*-BuCl. Subsequently, development of the Winstein Ion Pair Scheme introduced additional steps (ionization to an internal ion pair followed by initial dissociation to a solvent separated ion pair) either of which could be rate determining. Bentley and coworkers defined a new Y scale based upon 2-AdOTs solvolyses, by postulating that the ionization step leading to the formation of intimate ion pair is rate determining and proceeds without significant internal return. However, several studies suggested that the solvent-separated ion pair is involved in the slow step.^{38,39,57}

Paradisi and Bunnett have shown that in aqueous ethanol, acetic acid, and trifluoroacetic acid media the rate of ¹⁸O exchange in unsolvolyzed 2-adamantyl benzenesulfonate is faster than the rate of solvolysis.²⁵ This result strongly suggests that internal return does occur and C-O bond cleavage is not rate determining.

Jencks³³ introduced a mechanism which involves rate-determining diffusional separation of an intimate ion pair accompanied by solvent capture of the cation leading to product formation, as shown below.³⁴

$$k_{-1} \gg k_1, k_{-1} > k_2$$

Consistent with this hypothesis are product ratios observed from the solvolysis of 1- and 2-AdOTs in ethanol-2,2,2-trifluoroethanol (TFE), which favor the TFE ether product over the entire range of binary solvent compositions.⁵⁹⁻⁶³ Apparently, the diffusional separation of the leaving group and the substrate is relatively slow i.e., the cation does not have a long enough lifetime to allow diffusion of the ion pair to approach the solvent separated stage. Therefore, at this stage, the cation can either return to the substrate (internal return) or react with whatever nucleophile is present. Because of the enhanced acidity of TFE relative to ethanol, it would be expected that the former would be favored in the ground state solvation shell around the sulfonate moiety, and also in the internal ion pair resulting from

C-O bond cleavage. Hence, in a rate-determining diffusional separation of the internal ion pair, TFE would also be favored in the product.

Correlation of Solvolysis Rates with Intrinsic Medium Properties

Despite the various attempts to correlate the physical and chemical solvent properties with empirical parameters (e.g., ionizing power and nucleophilicity), the exact role of solvent in these solvolyses is poorly understood. To date, essentially all empirical parameters developed to characterize solvent properties have been determined either directly (Y and N) or indirectly (c and d) from rate data measured in model substrates that are undergoing the very reaction that is being probed.³⁵ In other words, parameters such as Y are predicated upon an assumed mechanism and then used as a mechanistic probe in the same type of reaction on other substrates.

The major objective of this research is to study an alternative treatment for evaluating the solvolysis mechanism in terms of intrinsic medium properties and their dependence upon solvent composition. In light of the product studies mentioned above, and Jencks' model of rate-determining diffusional separation of specifically solvated internal ion pairs, intrinsic medium properties such as viscosity, molar volume, and density seemed to be promising candidates for investigation.

Viscosity-Diffusion Model

The coefficient of diffusion D , is defined as $D = kT/6\pi r\eta$, where k is the Boltzmann constant, T is the temperature, r is the radius of a spherical molecule and η is the coefficient of viscosity. Thus, diffusion is inversely proportional to viscosity. This suggests that if product formation is diffusionally controlled and occurs in the rate-determining step, then solvolysis rates may manifest some characteristic of the medium viscosity.

A relationship for the free energy of activation for viscous flow³⁶ ($F_{vis\#}$) is given in equation 17, where R is the gas constant, T is the temperature,

$$F_{vis\#} = \frac{RT \ln V\eta}{hN} \quad (17)$$

V is the molar volume, η is the viscosity, h is planck's constant and N is Avogadro's number.

Assuming that diffusional separation of specifically solvated internal ion pairs is rate determining in the solvolysis of simple alkyl substrates such as adamantyl, one can hypothesize that the activation free energy contains a component reflecting viscous flow. Thus, we can write expression 18,

$$\Delta F^\# \propto \Delta F_{vis.\#} \propto \log V\eta \propto \log k_{obs} \quad (18)$$

which leads to expression 19 when a reference state is included.

$$\log k/k_o \propto \log (V\eta/V_o\eta_o) \quad \text{or} \quad \log (V/V_o) + \log (\eta/\eta_o) \quad (19)$$

Combining a rate determining diffusional solvolytic process with equation 17 leads to the possibility that observed rates may correlate with medium molecular volume and/or viscosity.

For this work we chose to study the simple binary aqueous media: aqueous methanol, ethanol, acetone, dioxane, and TFE, for which there is a relatively large number of substrates whose rates have been determined over a wide range of solvent composition, as well as ample density and viscosity data, all measured at 25 °C. Further, since water is a common cosolvent, it can be used conveniently as a reference state (k_o , V_o , and η_o). For our initial work we have ignored any viscosity contributions, and have focused on solvent molecular volume. The partial molar volume parameter $(V_m/PMV_{H_2O})_i$ was defined, where V_m is the molar volume of a particular solvent of composition i , and PMV_{H_2O} is the partial molar volume of water at the same composition. Reported below are the results of correlations of solvolysis rates with both medium composition (mole fraction) and the solvent molar volume parameter V_m/PMV_{H_2O} .

Treatment of the data

In all cases medium compositions were converted from either volume percent or weight percent to mole fraction, and expressed in terms of the mole fraction of water. All data used were determined at 25 °C unless otherwise noted. All calculations and correlations were performed on computer using the UCALC³⁷ program.

The solvent molar volume parameter was calculated from density data. Several sets of density data were available for most of the solvent systems studied. Data sets for aqueous methanol (6), ethanol (7), acetone(6) and dioxane (3) were taken from Timmermans compilation.⁴⁰ A single data set for 2,2,2-trifluoroethanol-water (TFE-H₂O) was reported by Murto and Heino.⁵⁶ For each set, average molar volumes, partial molar volumes, and the solvent molar volume parameters (V_m/PMV_{H_2O}) were calculated at the solvent compositions reported. The results were correlated with the mole fraction of water (X_{H_2O}), using the third order polynomial equation (20).

$$V_m = a_0 + a_1 X_{H_2O} + a_2 X_{H_2O}^2 + a_3 X_{H_2O}^3 \quad (20)$$

The V_m and V_m/PMV_{H_2O} values at the solvent compositions for which rate data were determined were analytically interpolated from equation 20. A few sets gave anomalous results and were rejected. The consistent sets (ethanol, 5; methanol, 3; acetone, 6; dioxane, 3) were averaged to give the resulting V_m and V_m/PMV_{H_2O} values which are listed in Table I, and which were used in subsequent correlations. Most of the sets that gave anomalous results either had relatively few data points, or were determined over a narrow composition range.

The logarithms of specific solvolysis rates for a variety of substrates were plotted versus the mole fraction of water, and the resulting plots were used as a reference to benchmark the dispersion phenomenon in terms of the water reference state. Similar plots were constructed for the $\log k_{obs}$ values versus $\log (V_m/PMV_{H_2O})$. In this case the data was correlated using equation 21.

$$\log (k/k_o) = s.\log (V_m/PMV_{H_2O}) \quad (21)$$

Correlation of Specific Rates of Solvolysis

The correlation results for 1-adamantyl substrates with a variety of leaving groups, namely, chloride (1-AdCl), bromide (1-AdBr), iodide (1-AdI), nitrate (1-AdONO₂), mesylate (1-AdOMs), tresylate (1-AdOTr), tosylate (1-

AdOTs), picrate (1-AdPicrate), chloroformate (1-AdOCOCl) and fluoroformate (1-AdOCOF), are listed in Table II. In Table III are listed results for correlations with 2-AdOTf, 2-AdOTr, 2-AdOTs, 2-AdOMs, 2-AdPFBS (pentafluorobenzenesulfonate), and 2-AdOCIO₃ (perchlorate). The correlation results for other systems including *t*-BuCl, *t*-butyl bromide (*t*-BuBr), α -phenylethyl chloride, α -phenylethyl bromide, neophyl chloride, neophyl bromide, benzhydryl chloride, benzhydryl bromide, methyl tosylate, methyl perchlorate and allyl tosylate are listed in Table IV.

RESULTS AND DISCUSSION

Evaluation of Mole Fraction - Log Rate Plots

The plot of log k_{obs} versus the mole fraction of water ($X_{\text{H}_2\text{O}}$) for the solvolyses of 1-AdBr in EtOH-H₂O, MeOH-H₂O, Ac-H₂O, Diox-H₂O and TFE-H₂O indicates that separate lines are observed for each solvent pair as shown in Figure 2. The rates increase with increasing water concentration and show a non-linear relationship with mole fraction of water. The significant rate enhancement in the less nucleophilic TFE media can be rationalized in terms of enhanced electrophilic assistance in the more acidic TFE solvent.

Comparison of the rate data at given water mole fraction reveals that the rates increase in the order $\text{Diox-H}_2\text{O} \approx \text{Ac-H}_2\text{O} < \text{EtOH-H}_2\text{O} < \text{MeOH-H}_2\text{O} < \text{TFE-H}_2\text{O}$. In other words, the rates increase in the order of the cosolvents $\text{Diox} \approx \text{Ac} < \text{EtOH} < \text{MeOH} < \text{TFE} < \text{H}_2\text{O}$. Ignoring acetone and dioxane which are non-hydroxylic and non-nucleophilic, the rates increase in a manner that does not parallel nucleophilicity, since the nucleophilicities of EtOH, MeOH, TFE and H₂O are 0.09, 0.01, -2.78, and -0.26 respectively.

Similar dispersion was observed in the log k versus $X_{\text{H}_2\text{O}}$ plots for all of the 1-adamantyl substrates listed in Table II (Figures 1 to 10). While the curvatures of the individual solvent systems were not characterized analytically, it appeared qualitatively that the curvatures were similar in a given solvent system for all substrates. On the other hand, curvatures differed noticeably amongst the various solvent systems. In other words, the curvature in aqueous ethanol plots was similar and relatively independent of the particular leaving group, yet the curvature in aqueous ethanol plots differed from that observed in corresponding aqueous methanol plots. Thus, the curvature was largely due to the nature of the medium and not the substrate which suggests that in these cases the dispersion magnitude does not necessarily reflect a mechanistic change.

Curvature and dispersion characteristics similar to the 1-adamantyl substrates also were observed for the corresponding 2-adamantyl compounds

listed in Table III (Figures 11 to 16). In addition, more pronounced examples of dispersion were observed for the other systems listed in Table IV (Figures 17 to 27). While a more detailed analytical treatment of the curvatures and dispersion magnitudes are of interest, we decided to focus our attention on correlations involving solvent molecular volume.

Correlations of Log k_{obs} with Log ($V_m/\text{PMV}_{\text{H}_2\text{O}}$)

As discussed above, Jencks' mechanistic model of rate determining diffusional separation of specifically solvated internal ion pairs for the solvolysis of simple alkyl substrates, coupled with the observed relationship between product composition and medium viscosity in the solvolysis of bridgehead sulfonates in TFE-EtOH media, suggested to us that observed rates may be related to medium viscosity and/or molecular volume. Plots of log k_{obs} versus the partial molar volume parameter defined earlier ($V_m/\text{PMV}_{\text{H}_2\text{O}}$) are shown in Figures 28 to 37 for 1-adamantyl substrates. Remarkably, in those cases where the leaving group is relatively small (Cl, Br, I, ONO_2 , OMs, and OTr), dispersion is not observed! Even for the larger tosylate and picrate leaving groups, dispersion is reduced significantly compared to the corresponding mole fraction plots. In the haloformates, where the mechanisms are not those of simple solvolyses, the plots are more complex. Results of the correlation of these data with equation 21, are listed

in Table II. Correlation coefficients for leaving groups described above as small were all ≥ 0.993 , and slopes are similar with an average value of -10.0 ± 0.7 . The linearity in the plots appears to be consistent with a constant mechanism.

Dispersion is significantly reduced in case of **1-AdOTs** and **1-AdPic** but not completely eliminated with low correlation coefficients which could be attributed to the large leaving groups involved. The poor correlation coefficients for the studies of **1-AdOCOCl** and **1-AdOCOF** can be interpreted in terms of the different mechanism associated with these systems as discussed earlier since the diffusional mechanism is not operating in these systems.

Thus, dispersion is successfully removed in case of **1-Ad** systems with relatively small and symmetrical leaving groups like **Cl**, **Br**, **I**, **ONO₂**, **OMs**, **OTr** as compared to large leaving groups such as **OTs** or **Pic** and the systems (**1-AdOCOCl** and **1-AdOCOF**) with different mechanism.

The results for the correlations on the **2-Ad** system are listed in Table III and the plots are shown in Figures 38 to 43. Dispersion is observed, but is significantly reduced in the partial molar volume parameter plots. The correlation coefficients are listed in Table III. The correlation coefficients are not as good as those obtained for **1-Ad** systems. Unlike **1-Ad**, where the reacting carbon is tertiary and the reaction is only feasible from a front-side,

ground state solvation and subsequent solvent attack on the incipient 2-Ad carbocation are possible on both the front-side and back-side attack on the reacting carbon. Thus, the 2-Ad system represents a composite of front-side solvation effects, as in the bridged 1-Ad cases, plus backside solvation which would not be expected to reflect the same solvent properties as on the front-side. For example, front-side solvation in the vicinity of the leaving group should be predicated on solvent-leaving group hydrogen bonding (solvent acidity), while backside solvation would reflect solvent nucleophilic properties.

The results of the correlations for a variety of other systems are listed in Table IV and the plots of the correlations are shown in Figures 44-54. Solvation in the vicinity of the reacting carbon is expected to be affected by additional variables. Some lead to resonance stabilized cations upon ionization, whose lifetimes may be sufficiently extended beyond the diffusional time domain to allow "back-side" solvation effects to become important on the front-side as well. Interestingly, dispersion was not observed in the *t*-butyl halides. In other cases like α -phenylethyl halides and neophyl halides, dispersion was significantly reduced over the mole fraction plots. The low correlation coefficients observed in case of benzhydryl halides can be attributed to the presence of two aromatic rings as compared to α -phenylethyl halides with only one aromatic ring present.

CONCLUSIONS

Correlations of solvolysis rates with the mole fraction of water strongly reinforces earlier conclusions that dispersion is a general phenomenon. The results of the rate versus partial molar volume parameter support the hypothesis that solvolysis rates can be correlated with intrinsic medium properties. Elimination of dispersion for simple 1-Ad systems is consistent with the mechanistic model of product formation via concomitant attack of solvent during the rate-limiting diffusional separation of specifically solvated intimate ion-pair intermediates.

The observation of variable dispersion in 1-Ad substrates containing more complex leaving groups, 2-Ad substrates, and a variety of systems that can lead to resonance stabilized, longer-lived intermediates interpreted in terms of overall solvation effects are a composite of several different solvent attributes such as acidity and nucleophilicity, and further complicated by the lifetime of the reacting species relative to the diffusional motion of the medium.

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Table I. Basis sets for $\log(V_m/PMV[H_2O])$ for all binary solvent mixtures^a at 25 °C.

E ^b	X ^c	p ^d	M ^e	X ^c	p ^d	A ^f	X ^c	p ^d	D ^g	X ^c	p ^d	T ^h	X ^c	p ^d
100	0	0.630	100	0	0.458	95	0.178	0.642	95	0.2	0.624	100	0	0.650
95	0.146	0.542	95	0.106	0.418	90	0.313	0.579	90	0.346	0.574	97	0.147	0.624
90	0.265	0.485	90	0.201	0.386	85	0.420	0.526	85	0.456	0.526	90	0.382	0.522
85	0.364	0.439	80	0.361	0.312	80	0.506	0.479	80	0.543	0.478	85	0.495	0.450
80	0.448	0.399	70	0.492	0.246	70	0.637	0.395	75	0.613	0.432	84.5	0.505	0.443
70	0.582	0.331	60	0.601	0.190	60	0.732	0.320	70	0.671	0.388	80	0.581	0.385
60	0.684	0.271	50	0.693	0.143	50	0.804	0.252	60	0.760	0.307	70	0.704	0.282
50	0.764	0.217	40	0.772	0.104	40	0.860	0.192	50	0.826	0.236	60	0.787	0.205
40	0.830	0.167	30	0.840	0.073	30	0.905	0.138	40	0.877	0.174	50	0.847	0.146
30	0.883	0.122	20	0.900	0.047	20	0.943	0.090	20	0.950	0.074	0	1	0
20	0.929	0.081	10	0.953	0.026	10	0.974	0.047	0	1	0			
10	0.997	0.043	0	1	0	5	0.987	0.027						
5	0.984	0.025				0	1	0						
0	1	0												

^a Average values for all aqueous solvents (ethanol, methanol, acetone, dioxane and TFE) from ref. 40. ^b Volume percent ethanol. ^c Mole fraction of water. ^d Partial molar volume function $\log(V_m/PMV[H_2O])$. ^e Volume percent methanol. ^f Volume percent acetone. ^g Volume percent dioxane. ^h Weight percent TFE.

Table II. Correlation of solvolyses of 1-Adamantyl systems

Substrates	r ^a	s ^b	n ^c	N ^d
1-AdCl ^e	0.994	-9.74	3	31
1-AdBr ^f	0.994	-11.3	4	32
1-AdI ^g	0.993	-8.62	3	30
1-Ad Nitrate ^h	0.993	-10.2	4	27
1-Ad Mesylate	0.996 ⁱ	-11.0	3	9
	0.994 ^j	-10.4	3	15
1-Ad Tresylate ^k	0.996	-9.40	2 ^l	5
1-Ad Tosylate ^m	0.942	-10.1	4	16
1-Ad Picrate ⁿ	0.958	-5.64	3	15
1-Ad Chloroformate ^o	0.828	-5.25	4	17
1-Ad Fluoroformate ^p	0.910	-5.23	4	14

^a Correlation coefficient. ^b Slope. ^c All sets containing ethanol-water, methanol-water and acetone-water unless stated otherwise, 4 solvents signify ethanol-water, methanol-water, acetone-water and dioxane-water.

^d Number of points; total points on the plot. ^e Rate data from ref. 11. ^f Data from ref. 11 and 22. ^g ref. 41. ^h ref. 42. ⁱ ref. 43. ^j Additional values from ref. 44. ^kref.45. ^l 2sol. include ethanol-water and acetone-water. ^m ref. 46. ⁿ ref. 47.

^oref.32.^pref.31.

Table III. Correlation of solvolyses of 2-Adamantyl systems

Substrates	r ^a	s ^b	n ^c	N ^d
2-Ad Triflate	0.967 ^e	-8.60	3	13
	0.902 ^f	-6.99	3	16
2-Ad Tresylate	0.987 ^g	-9.19	4	16
	0.981 ^g ₁	-8.50	4	19
	0.994 ^h	-8.20	2 ^q	6
2-Ad Tosylate	0.988 ⁱ	-8.57	2 ^p	9
	0.989 ^j	-9.70	3	14
2-Mesylate ^k	0.997	-9.99	2 ^l	8
2-Ad PFBS ^m	0.956	-8.09	4	16
2-Ad Perchlorate	0.832 ⁿ	-6.80	4	20
	0.886 ^o	-6.53	3	16

^{a-d} Same as table 2. ^e ref. 47. ^f ref. 48. ^g second set with additional values from ref. 49. ^h ref. 45. ⁱ ref. 8, 9 and 43. ^j Additional values from ref. 50. ^k ref. 50 and 44. ^l 2 sol. include ethanol-water and acetone-water. ^m ref. 51. ⁿ ref. 52. ^o ref. 47. ^p Ethanol-water and methanol-water. ^q Ethanol-water and acetone-water.

Table IV. Correlation of solvolyses of other Alkyl systems

Substrates	r ^a	s ^b	n ^c	N ^d
t-BuCl ^e	0.994	-9.26	4	41
t-BuBr ^f	0.994	-8.49	4	28
α -PhenylethylCl ^g	0.984	-9.74	3	25
α -PhenylethylBr ^h	0.982	-8.80	3	22
Neophyl Chloride ⁱ	0.982	-8.37	3	15
Neophyl Bromide ⁱ	0.983	-7.74	3	19
BenzhydrylCl ^j	0.805	-8.24	4	14
BenzhydrylBr ^j	0.936	-10.0	2 ^l	6
Methyl Tosylate ^k	0.930	-2.75	4	26
Methyl Perchlorate ^m	0.614	-0.74	4	44
Allyl Tosylate ⁿ	0.959	-4.67	4	24

^{a-d} Same as table 2. ^e ref. 16. ^f ref. 18. ^g ref. 17. ^h ref. 18. ⁱ ref. 19. ^j ref. 20.

^k ref. 9. ^l Acetone-water and dioxane-water. ^m ref. 54. ⁿ ref. 55.

Figure 1. Plot of log rate of 1-AdCl vs. mole fraction of water (X_{H_2O}).

Figure 2. Plot of log rate of 1-AdBr vs. mole fraction of water (X_{H_2O}).

Figure 3. Plot of log rate of 1-AdI vs. mole fraction of water (X_{H_2O}).

Figure 4. Plot of log rate of 1-AdONO₂ vs. mole fraction of water (X_{H_2O}).

Figure 5i. Plot of log rate of 1-AdOMs vs. mole fraction of water (X_{H_2O}).

Figure 5j. Plot of log rate of 1-AdOMs vs. mole fraction of water (X_{H_2O}).

Figure 6. Plot of log rate of 1-AdOTr vs. mole fraction of water (X_{H_2O}).

Figure 7. Plot of log rate of 1-AdOTs vs. mole fraction of water (X_{H_2O}).

Figure 8. Plot of log rate of 1-Ad picrate vs. mole fraction of water (X_{H_2O}).

Figure 9. Plot of log rate of 1-AdOCOCl vs. mole fraction of water (X_{H_2O}).

Figure 10. Plot of log rate of 1-AdOCOF vs. mole fraction of water (X_{H_2O}).

Figure 11e. Plot of log rate of 2-AdOTf vs. mole fraction of water (X_{H_2O}).

Figure 11f. Plot of log rate of 2-AdOTf vs. mole fraction of water (X_{H_2O}).

Figure 12g. Plot of log rate of 2-AdOTr vs. mole fraction of water (X_{H_2O}).

Figure 12g1. Plot of log rate of 2-AdOTr vs. mole fraction of water (X_{H_2O}).

Figure 12h. Plot of log rate of 2-AdOTr vs. mole fraction of water.

Figure 13. Plot of log rate of 2-AdOTs vs. mole fraction of water (X_{H_2O}).

Figure 14. Plot of log rate of 2-AdOMs vs. mole fraction of water (X_{H_2O}).

Figure 15. Plot of log rate of 2-Ad PFBS vs. mole fraction of water (X_{H_2O}).

Figure 16n. Plot of log rate of 2-AdOClO₃ vs. mole fraction of water (X_{H_2O}).

Figure 16o. Plot of lot rate of 2-AdOClO₃ vs. mole fraction of water (X_{H_2O}).

Figure 17. Plot of log rate of $t\text{-BuCl}$ vs. mole fraction of water (X_{H_2O}).

Figure 18. Plot of log rate of $t\text{-BuBr}$ vs. mole fraction of water (X_{H_2O}).

Figure 19. Plot of log rate of α -Phenylethyl Chloride vs. mole fraction of water (X_{H_2O}).

Figure 20. Plot of log rate of α -Phenylethyl Bromide vs. mole fraction of water (X_{H_2O}).

Figure 21. Plot of log rate of Neophyl Chloride vs. mole fraction of water (X_{H_2O}).

Figure 22. Plot of log rate of Neophyl Bromide vs. mole fraction of water (X_{H_2O}).

Figure 23. Plot of log rate of Benzhydryl Chloride vs. mole fraction of water (X_{H_2O}).

Figure 24. Plot of log rate of Benzhydryl Bromide vs. mole fraction of water (X_{H_2O}).

Figure 25. Plot of log rate of Methyl Tosylate vs. mole fraction of water (X_{H_2O}).

Figure 26. Plot of log rate of Methyl Perchlorate vs. mole fraction of water (X_{H_2O}).

Figure 27. Plot of log rate of Allyl Tosylate vs. mole fraction of water.

Figure 28. Plot of log rate of 1-AdCl vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 29. Plot of log rate of 1-AdBr vs. log partial molar volume parameter (V_m/PMV_{H_2O}).

Figure 30. Plot of log rate of 1-AdI vs. log partial molar volume parameter ($V_m / \text{PMV}_{\text{H}_2\text{O}}$).

Figure 31. Plot of log rate of 1-AdONO₂ vs. log partial molar volume parameter (V_m/PMV_{H_2O}).

Figure 32i. Plot of log rate of 1-AdOMs vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 32j. Plot of log rate of 1-AdOMs vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 33. Plot of log rate of 1-AdOTr vs. log partial molar volume parameter (V_m/PMV_{H₂O}).

Figure 34. Plot of log rate of 1-AdOTs vs. log partial molar volume parameter (V_m/PMV_{H₂O}).

Figure 35. Plot of log rate of 1-Ad picrate vs. log partial molar volume parameter (V_m/PMV_{H_2O}).

Figure 36. Plot of log rate of 1-AdOCOCl vs. log partial molar volume parameter (V_m/PMV_{H_2O}).

Figure 37. Plot of log rate of 1-AdOCOF vs. log partial molar volume parameter (V_m/PMV_{H_2O}).

Figure 38e. Plot of log rate of 1-AdOTf vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 38f. Plot of log rate of 2-AdOTf vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 39g. Plot of log rate of 2-AdOTr vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 39g1. Plot of log rate of 2-AdOTr vs. log partial molar volume parameter ($V_m / \text{PMV}_{\text{H}_2\text{O}}$).

Figure 39h. Plot of log rate of 2-AdOTr vs. log partial molar volume parameter (V_m/PMV_{H₂O}).

Figure 40. Plot of log rate of 2-AdOTs vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 41. Plot of log rate of 2-AdOMs vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 42. Plot of log rate of 2-Ad PFBS vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 43n. Plot of log rate of 2-AdOClO₃ vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 43o. Plot of log rate of 2-AdOClO₃ vs. log partial molar volume parameter (V_m/PMV_{H_2O}).

Figure 44. Plot of log rate of t-BuCl vs. log partial molar volume parameter (V_m/PMV_{H_2O}).

Figure 45. Plot of log rate of t-BuBr vs. log partial molar volume parameter (V_m/PMV_{H_2O}).

Figure 46. Plot of log rate of α -Phenylethyl Chloride vs. log partial molar volume parameter (V_m/PMV_{H_2O}).

Figure 47. Plot of log rate of α -Phenylethyl Bromide vs. log partial molar volume parameter (V_m/PMV_{H_2O}).

Figure 48. Plot of log rate of Neophyl Chloride vs. log partial molar volume parameter (V_m/PMV_{H_2O}).

Figure 49. Plot of log rate of Neophyl Bromide vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 50. Plot of log rate of Benzhydryl Chloride vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 51. Plot of log rate of Benzhydryl Bromide vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 52. Plot of log rate of Methyl Tosylate vs. log partial molar volume parameter (V_m/PMV_{H₂O}).

Figure 53. Plot of log rate of Methyl Perchlorate vs. log partial molar volume parameter ($V_m/\text{PMV}_{\text{H}_2\text{O}}$).

Figure 54. Plot of log rate of Allyl Tosylate vs. log partial molar volume parameter (V_m/PMV_{H_2O}).