

Limitations of the Transition State Variation Model(5) Dual Reaction Channels for Solvolysis of Dansyl Chloride

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Rate of solvolysis of dansyl chloride in aqueous binary mixtures of acetone, methanol and ethanol are reported. Kinetic solvent isotope effects in methanol and product selectivities in alcohol-water mixtures are also reported. Kinetic data are interpreted with the Grunwald-Winstein and Kivinen equations. The value of $k_{\text{CH}_3\text{OH}}/k_{\text{CH}_3\text{OD}} = 1.76$ suggests that a general have catalyzed and/or an $S_{\text{A}}\text{N}$ pathway is operative in methanol, a less polar solvent. Rate-rate profiles for solvolysis of dansyl chloride in the aqueous binary media indicate a change in reaction channel from $S_{\text{A}}\text{N}$ (in less polar media) to $S_{\text{N}}2$ (in more polar media) mechanism.

Introduction

Dispersions in the Grunwald-Winstein plots present difficulties for quantitative analysis of the solvolysis data in binary solvent mixtures.¹ The model compounds usually adopted for the Grunwald-Winstein equation, Eq. (1), are *t*-butyl chloride, 1- and 2-adamantyl chlorides.²

$$\log(k/k_0)_{\text{RX}} = mY \quad (\text{or } mY_X) \quad (1)$$

Dispersion phenomena arise often with the solvolytic rate data of aromatic substrates in a series of binary mixtures in the form of separate dispersion lines or curves. Interpretation of such dispersions in the Grunwald-Winstein plots by the transition state (TS) variation model alone presents serious limitations.³⁻⁵ The dispersion may originate from a mechanistic change or general base catalysis⁶ due to various effects, e.g., ion pair return,⁷⁻⁹ nucleophilic solvent assistance^{8,10} and anchimeric assistance.¹¹

The solvent effects on the rates of aliphatic model compounds which are used for the determination of ionizing power scale, Y_X , are expected to differ from those on the rates of aromatic model compounds for which the Y_X scale is actually applied. For example, the stabilities of benzylic and aromatic carbonyl carbo-cations are strongly influenced by the conjugative charge delocalization into the benzene ring. This provides an example of dispersion in the Grunwald-Winstein plots due to the solvent effect on the conjugation of reaction center with the benzene ring in the TS, i.e., a general specific solvent effect, and requires a more detailed investigation in order to understand the mechanistic changes associated with the dispersion behavior.

In many mechanistic studies using the Grunwald-Winstein plots, this type of general specific solvent effect has not been taken into account adequately, reacting sometimes risky conclusions. We have reported recently on the solvolysis studies involving sulfonyl compounds in order to shed some lights on these problems.^{5,12} As a continuation of the work to this effect, we determined solvolysis rates of dansyl chloride (1-*N,N*-dimethylaminonaphthalene-5-sulfonyl chloride) in MeOH-H₂O, EtOH-H₂O and acetone-H₂O mixtures and solvent isotope effects in methanol. We have also determined product selectivities in the MeOH-H₂O and EtOH-H₂O media.

Experimental

Materials. Tokyo Kasei GR grade dansyl chloride and Merck GR methanol, ethanol and acetone were used without further purification. Double distilled water was redistilled in the presence of KMnO₄ and the portion with conductivity less than 20 μmhos was used. The conductivity water was obtained by treating double distilled water with ion exchange resin, which had specific conductivity less than 1×10^6 mho cm^{-1} .

Kinetic Procedure. In order to overcome precipitation and mixing problems in water-rich media, platinum cell (5 ml) with Turbo-stirrer was used. For rate measurements of fast reactions, an IBM-XT/AT interfaced with A/D converter was used and to improve reproducibility and consistency the data were treated with a personal computer.¹² The pseudo-first order rate constants were determined using the LSKIN program. Temperature was kept to $\pm 0.05^\circ\text{C}$.

Product Selectivity. Product selectivities in EtOH-H₂O and MeOH-H₂O mixtures were determined with an HPLC, which has been described in detail previously.¹³⁻¹⁵ The concentration of solvolysis products, sulfonic acid and sulfonyl ester, were determined by the HPLC and the selectivity values, *S*, were estimated by Eq. (2) after correcting the concentration using calibration curves.^{1,13-15}

$$S = [\text{ester product}][\text{water}]/[\text{sulfonic acid}][\text{alcohol}] \quad (2)$$

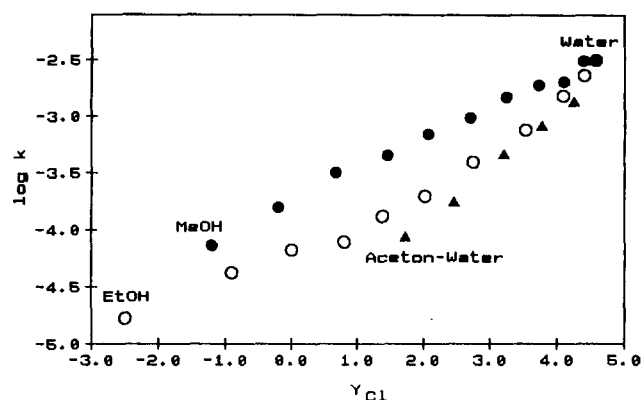
The two products were confirmed using H-NMR. In order to improve resolution and to adjust proper retention time, 80% MeOH-H₂O was used as eluting solvent and flow rate was adjusted to 1 ml min^{-1} . The wave length of UV detector was set to 272.5 nm.

Results and Discussion

The rate constants for solvolyses of dansyl chloride in EtOH-H₂O, MeOH-H₂O and acetone-H₂O mixtures at 25.0°C are summarized in Table 1. Reference to Table 1 reveals that the rate increases in the order Acetone-H₂O < EtOH-H₂O < MeOH-H₂O and with the increase in the water content of the mixtures; this means that the rate is accelerated by a solvent with higher ionizing power, *Y*, suggesting the im-

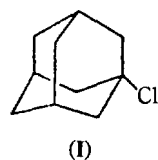
Table 1. Rate Constants (k) for Solvolyses of Dansyl Chloride in Aqueous Binary Mixtures at 25°C

| Solvent % (V/V) | $k/10^{-4} \text{ s}^{-1}$ | | |
|--------------------|----------------------------|----------|---------|
| | Ethanol | Methanol | Acetone |
| 100 | 0.168 | 0.735 | |
| 90 | 0.424 | 0.58 | |
| 80 | 0.669 | 3.17 | |
| 70 | 0.789 | 4.50 | |
| 60 | 1.32 | 6.92 | |
| 50 | 1.98 | 9.75 | 0.886 |
| 40 | 3.93 | 14.8 | 1.78 |
| 30 | 7.62 | 18.8 | 4.67 |
| 20 | 15.2 | 20.2 | 8.33 |
| 10 | 23.0 | 31.0 | 13.6 |
| H ₂ O | 31.5 | 31.5 | 31.5 |

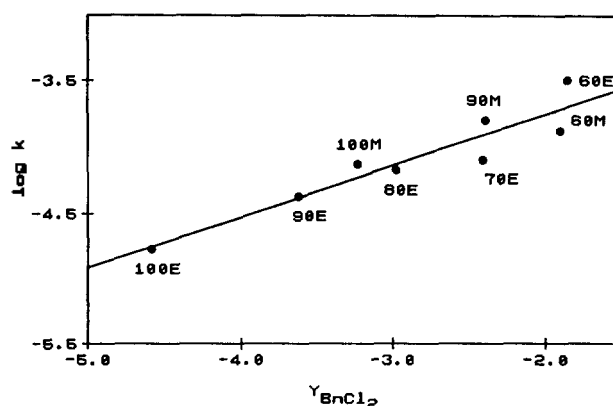
**Figure 1.** Correlation of logarithms of solvolysis rates for dansyl chloride at 25°C versus Y_{Cl} (Y_{Cl} data from ref. 16).

portance of bond breaking in the TS.

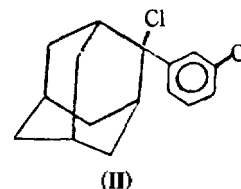
The Grunwald-Winstein plots of the rates in Table 1 are present in Figure 1 using the ionizing power scale, Y_{Cl} , of Bentley *et al.*, based on 1-adamantyl chloride, (I).^{11,16} Examination of Figure 1 shows that the plots for the three aqueous



mixtures exhibit dispersion into three separate family of lines. This constitutes evidence against single mechanism for all the aqueous mixtures; if the solvolysis were to proceed by a single mechanism, all the points in Figure 1 should have fallen into a single straight line. A similar dispersion was, however, observed in the plots of rate constants for nucleophilic substitution of benzoyl systems. Bentley *et al.*, have pointed out that this type of scatter in the Grunwald-Winstein plots can not be ascribed to the simple solvent effect, but may represent a mechanistic change.^{15,13-16} Another possible cause for the scatter could be the different solvation behavior of the charge that is developing on the aromatic substrate from that on the aliphatic standard com-

**Figure 2.** Correlation of logarithms of solvolysis rates for dansyl chloride at 25°C versus Y_{BnCl_2} (Y_{BnCl_2} data from ref. 17).

pounds used for the determination of Y or Y_{Cl} scale. In order to test this possibility Liu *et al.*, suggested a new ionizing power scale, Y_{BnCl_2} , based on a standard compound [3'-chlorophenyl-2-chloroadamantane, (II)] with an aromatic ring into which the developing charge can delocalize.¹⁷



The $\log k$ vs. Y_{BnCl_2} plots using the k values obtained in this work, indeed, display a better linear relation ($r=0.938$) as shown in Figure 2. We note that only a limited number of Y_{BnCl_2} values are available and hence only a few points are seen in Figure 2, due to poor solubility of the standard compound in water-rich mixtures. A better linearity found in Figure 2 appears to support the view that the developing charge in the TS delocalizes into the aromatic ring, in both the substrate, dansyl chloride, and the standard compound, (II).

The slope of the plot in Figure 2, $m=0.38$, is relatively small and indicates that the reaction proceeds through a bimolecular mechanism, at least in the solvent media of relatively low ionizing power used in the plot. As mentioned above, due to a poor solubility of the standard compound (II), the Y_{BnCl_2} values are not available for the water-rich part, *i.e.*, highly ionizing part, of the aqueous mixtures.

Considerable dispersion into separate lines for various binary mixtures, as in Figure 2 can be rationalized by the two different aspects of solvent effect contributing to the solvolysis in different degree depending on the mechanism. For an S_N2 process, the rate will be more sensitive to the solvent ionizing power, Y_{Cl} , since bond breaking is important in the S_N2 mechanism, whereas for an addition-elimination ($S_A N$) process, the rate will be more sensitive to the nucleophilicity of the solvent, and the solvent molecules will act as a general base catalyst, since in this case bond formation is important. Reference to Figure 1 reveals that the plot of logarithm of rate constants for solvolyses of dansyl chloride versus Y_{Cl} values shows only a small dispersion into separate lines for the three water-rich parts of binary mix-

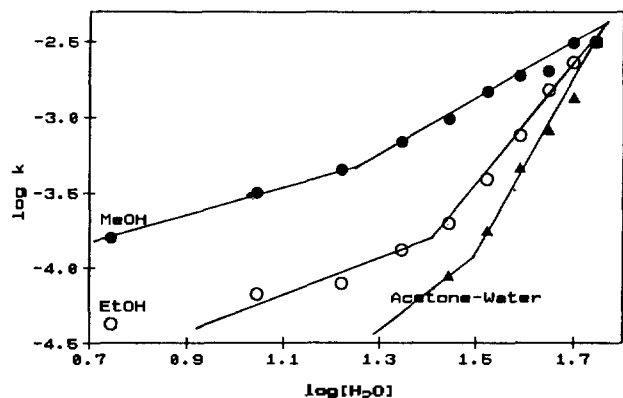
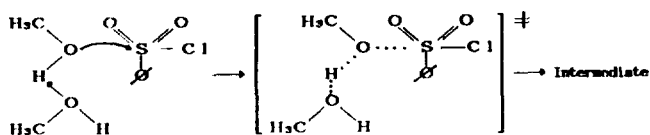


Figure 3. Correlation of solvolysis rates for dansyl chloride at 25°C versus $\log [H_2O]$.



Scheme 1.

tures, converging to a point corresponding to the pure water. Thus in the water-rich solvent mixtures with relatively high ionizing power the reaction is likely to proceed by the S_N2 TS, while in contrast in the less ionizing cosolvent-rich solvent mixtures the reaction is more prone to the addition-elimination ($S_A N$) mechanism for which the effect of nucleophilicity of the solvent is more important than that of the leaving ability of leaving group.

A plot of logarithm of rate constants versus logarithm of water concentration, a Kivinen type plot,¹⁸ is shown in Figure 3 for the three aqueous mixtures. Examination of this Figure clearly shows two linear parts joined together for each aqueous binary mixtures; the slopes (n) of the linear parts change from low to high water content as 0.88→1.43 for MeOH, 1.69→4.14 for EtOH and 2.1→4.83 for acetone mixtures. This change in the slope can be ascribed to a mechanistic change reflected in the change of solvent participation in the TS. The increase in the slope of the Kivinen type of plots from low to high water content binary mixtures is again an indication of the mechanistic change from a bimolecular mechanism in which bond formation is relatively important ($S_A N$)¹⁹ to the one where bond breaking is important, (S_N2).

The solvent isotope effect in MeOH was relatively large, $k_{CH_3OH}/k_{CH_3OD}=1.76$ ($k_{CH_3OH}=7.18 \times 10^{-5} \text{ sec}^{-1}$ and $k_{CH_3OD}=4.09 \times 10^{-5} \text{ sec}^{-1}$), implying that the OH bond breaks partially in the TS. This is another piece of evidence in support of the $S_A N$ mechanism in MeOH in which a MeOH molecules acts as a general base catalyst, as shown in Scheme 1.

Selectivity values, S , (Eq. 2) for the solvolyses of dansyl chloride in aqueous alcohol binary mixtures are given in Table 2.

We note in the Table that a reversal in the trend of product selectivities occurs in both binaries at ca. 50% (v/v) H_2O content; the selectivity values, S , increase initially as the water content of the binaries increases until at about 50% H_2O reaching to a maximum value, $S=3, 4$ for MeOH

Table 2. Product Selectivities (S , Eq. 2) for Solvolysis of Dansyl Chloride in a Alcohol/Water Mixtures at 25°C

| Alcohol (%v/v) | Methanol | | Ethanol | |
|-------------------|--------------|-----|----------------|-----|
| | (Ester/Acid) | S | (Ester)/(Acid) | S |
| 90 | 6.68 | 1.7 | 4.87 | 1.8 |
| 80 | 3.82 | 2.1 | 3.09 | 2.5 |
| 70 | 2.51 | 2.4 | 2.41 | 3.4 |
| 60 | 6.16 | 3.2 | 1.84 | 4.0 |
| 50 | 1.48 | 3.4 | 1.33 | 4.3 |
| 40 | 0.939 | 3.2 | 0.88 | 4.3 |
| 30 | 0.560 | 2.9 | 0.50 | 3.8 |
| 20 | 0.324 | 2.9 | 0.19 | 2.5 |
| 10 | 0.106 | 2.2 | 0.064 | 1.9 |
| 5 | 0.035 | 1.5 | 0.028 | 1.7 |

and $S=4, 3$ for EtOH. The reactivity-selectivity principle (RSP) is violated in the low water region, whereas it is held in the high water region. In the low water region, the selectivity, and hence the ester product from the nucleophilic attack by a more nucleophilic alcohol molecule, increases with water content indicating that bond formation by the nucleophilic attack ($S_A N$) is more important in the TS in this region, in contrast, however, in the high water region the selectivity decreases with the increase in water content accompanied by an increase in the ionizing power, Y , indicating that bond breaking step gains more importance (S_N2) in this region.

In conclusion, the dispersions in the Grunwald-Winstein plots into separate lines for various binary mixtures in the low water region, changes in the slopes of the Kivinen type plots, the relatively large solvent isotope effect in MeOH and the maximum behavior in the product selectivity values in the aqueous alcohol binaries lead us to support a two-channel mechanism of $S_A N-S_N2$ for the solvolysis of dansyl chloride in aqueous binaries mixtures.

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Theory of Diffusion-Influenced Bimolecular Reactions in Solution: Effects of a Stochastic Gating Mode

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We have investigated the kinetics of diffusion-influenced bimolecular reactions in which one reactant has an internal mode, called the gating mode, that activates or deactivates its reactivity intermittently. The rate law and an expression for the time-dependent rate coefficient have been obtained from the general formalism based on the hierarchy of kinetic equations involving reactant distribution functions. The analytic expression obtained for the steady-state reaction rate constant coincides with the one obtained by Szabo *et al.*, who derived the expression by employing the conventional concentration-gradient approach. For the time-dependent reaction rate coefficient, we obtained for the first time an exact analytic expression in the Laplace domain which was then inverted numerically to give the time-domain results.

Introduction

When the inherent reaction step proceeds very rapidly upon the contact of reactant molecules, the diffusive encounter rate can influence the overall reaction rate. Examples can be found in radical or ion recombination reactions,^{1,2} intermolecular energy transfer reactions,^{3,4} enzyme-substrate reactions,⁵ tunneling reactions of solvated electrons,⁶ and the coagulation of colloid particles.⁷

A theory for the rate of diffusion-controlled reactions was first formulated by Smoluchowski.⁷ Since then the theory has been refined and generalized in many aspects⁸: *e.g.*, refined modelings of the reaction event by the radiation boundary condition⁹ or by the reaction sink function,¹⁰ rigorous formulations of the rate theory based on hierarchical kinetic equations governing the evolution of reactant molecule distribution,^{11,12} inclusion of the effects due to long-range intermolecular forces¹³ and solvent-mediated hydrodynamic interactions,¹⁴ consideration of orientation-dependent reactivity of reactant molecules,^{15,16} and so on.

An interesting generalization of the theory that has attracted much attention recently is to include the effect of structural fluctuation in reactant molecules that may dynamically alter their intrinsic reactivity.¹⁷⁻¹⁹ In enzyme-substrate reactions, for example, the enzyme molecule may have side

chains that can change the binding site accessibility. Motions of such side chains constitute a *gating mode* which *opens* and *closes* the binding site of substrate molecules.

One of the simplest model of gated diffusion-influenced reactions is that proposed by A. Szabo *et al.*¹⁹ They considered a bimolecular reaction between molecules of species *A* and *B*,



where *B* molecules, which do not change in the course of reaction like an enzyme in enzyme-substrate reactions, have a fluctuating reactivity due the gating dynamics of an internal mode. For simplicity, they assumed that the fluctuations in the reactivity of *B* molecules can be described as a two-state process and that the dynamics of the gate between the two states, open and closed, can be described by the first-order rate equation



Here we designate the *B* molecules in the open state as molecules *O* while those in the closed state as molecules *C*. k_c and k_o are the rate constants, respectively, for the closing and opening of the gate. Molecules of species *A* can react only with molecules *O*: