

Transition-State Variation in the Solvolyses of Phenyl Chlorothionoformate in Alcohol-Water Mixtures

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Solvolyses of phenyl chlorothionoformate in water, D₂O, CH₃OD, 50% D₂O-CH₃OD, and in aqueous binary mixtures of acetone, ethanol and methanol are investigated at 25.0 °C. The Grunwald-Winstein plots of first-order rate constants for phenyl chlorothionoformate with Y_{Cl} (based on 2-adamantyl chloride) show a dispersion phenomenon, and also the extended Grunwald-Winstein plots show a poor correlation for the solvolyses of phenyl chlorothionoformate. The ring parameter (I) has been shown to give considerable improvement when it is added as an hI term to the original and extended Grunwald-Winstein correlations. The dispersions in the Grunwald-Winstein correlations in the present studies are caused by the conjugation between the reaction center and the aromatic ring in the vicinity of the reaction center. This study has shown that the magnitude of I and m values associated with a change of solvent composition leads to predict the S_N2 transition state. The kinetic solvent isotope effects determined in deuterated water and methanol are consistent with the proposed mechanism of the general base catalyzed S_N2 mechanism.

Introduction

The phenomenon of "dispersion" in Grunwald-Winstein plots (eqn. 1) has, for many years, plagued quantitative interpretations of rate-rate profiles for solvolytic reactions in binary aqueous mixtures.¹⁻⁵

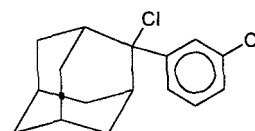
$$\log(k/k_o) = mY + c \quad (1)$$

In equation (1), k and k_o are specific rates of solvolysis substrate in a given solvent, of solvent ionizing power Y , and in 80% ethanol, respectively, m is the sensitivity of the substrate to changes in Y values, and c is a residual (constant) term. Equation (1) is commonly written without the intercept (c), which is not required for typical interpretations, but it is often considered as a "hidden" adjustable parameter in the correlations.⁶ In general, dispersion effects in unimolecular solvolyses^{7,8} make smaller contribution to the overall linear free energy relationship (LFER) than solvent nucleophilicity effects in bimolecular solvolyses. It was suggested that a second term which is governed by the sensitivity I of the substrate to solvent nucleophilicity N , should be added to equation (1) for bimolecular solvolyses. The resulting equation (2) is often referred to as an extended Grunwald-Winstein equation.⁹

$$\log(k/k_o) = mY + IN \quad (2)$$

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 compounds used for the determination of Y or Y_{Cl} scale. In order to test this possibility, Liu *et al.* suggested^{10,11} a new ionizing power scale, Y_{BrCl_2} , based on a standard compound [3'-chlorophenyl-2-chloroadamantane, (I)] with an aromatic ring in which the developing charge can delocalize. Fairly good lin-

ear relationships were observed in the logarithms of solvolytic rate constants of dansyl chloride and 2-thiophene-sulfonyl chloride vs. Y_{BrCl_2} , by Koo *et al.*^{12,13} These results suggested that the resonance contribution of the α -aryl group in the transition state plays an important role.¹¹



(I)

Kevill *et al.* recently suggested^{14,15} that, since the dispersion seems to follow a consistent pattern, it should be possible to develop an aromatic ring parameter (I), which, as qualified by the appropriate sensitivity (h), can be added to equations (1) or (2) to give equations (3) or (4), respectively.

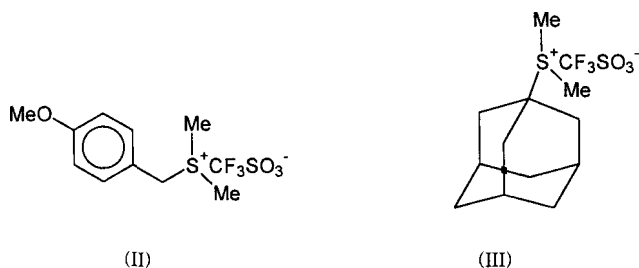
$$\log(k/k_o) = mY + hI + c \quad (3)$$

$$\log(k/k_o) = IN + mY + hI + c \quad (4)$$

A scale of I values was developed^{14,15} based on differences in the nature of the variations of the specific rates of solvolyses of the *p*-methoxybenzylidimethylsulfonium ion (II)^{16,17,18} and of the 1-adamantylidimethylsulfonium ion (III)¹⁹ (no aromatic ring) as the solvent composition was altered [equation (5)].

$$I = \log(k/k_o)_{p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{S}^+\text{Me}_2} - 1.3 \log(k/k_o)_{1\text{-AdS}^+\text{Me}_2} \quad (5)$$

Several other techniques, such as F/Cl leaving group effects,^{20,21} Hammett treatments of substituent effects,²²⁻²⁴ solvent isotope effect,²³⁻²⁵ and consideration of the activation parameters,²³⁻²⁵ had previously been applied to the studies of solvolyses of phenyl chloroformate,²³ phenyl chlorothioformates,^{23,26} chlorothionoformate and chlorodithionoformate

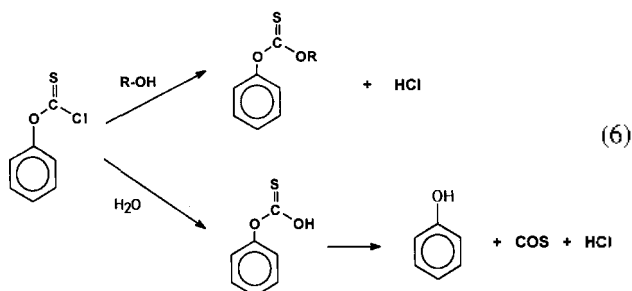


ester.²⁷ These techniques have indicated a bimolecular mechanism, almost certainly of the addition-elimination for the solvolyses of phenyl chloroformates²⁴ and phenyl chlorothioformates,²⁶ and have indicated S_N1 mechanism for the hydrolyses of chlorothioformate and chlorodithioformate ester.²⁷

In this work, dispersion phenomenon and reaction mechanism for the solvolysis of phenyl chlorothioformate in ethanol-water, methanol-water and acetone-water mixtures are investigated by applying the extended Grunwald-Winstein equation and aromatic ring parameter (ρ).

Results and Discussion

Rate constants for solvolysis of phenyl chlorothioformate [eqn. (6)]^{20-23,25} in aqueous binary mixtures of acetone, ethanol, methanol, deuterated water (D_2O) and methanol (CH_3OD) are reported in Table 1.



Rate constants increase in the order acetone- H_2O < EtOH- H_2O < MeOH- H_2O , and show a maximum rate near 30% methanol-water (30M). The rate increases slowly as the

Table 1. Rate constants (k , s^{-1}) for solvolyses of phenyl chlorothioformate in aqueous binary mixtures at 25 °C

v/v %	MeOH	EtOH	Acetone
	$k \times 10^4$		
100	1.72	0.326	-
90	2.74	0.578	-
80	3.69	0.715	0.0616
70	4.65	0.825	0.110
60	5.72	1.00	0.201
50	6.94	1.28	0.332
40	8.04	1.92	0.608
30	8.52	3.14	1.17
20	8.16	4.41	2.23
10	6.81	4.77	3.56
H_2O	5.27	5.27	5.27

water content of mixtures increases; this means that rate is slightly accelerated by solvent with higher ionizing power, Y , suggesting that bond breaking in the transition state is of little importance.

The Grunwald-Winstein plots [equation (1)] of the rates in Table 1 for solvolysis of phenyl chlorothioformate are presented in Figure 1 using the solvent ionizing power scale Y_{Cl} , based on solvolyses of 1-adamantyl chloride.²⁸ Examination of the figure shows that the plots for the three aqueous mixtures exhibit dispersions into three separate curves with maximum rate constants at near 30M in aqueous methanol mixtures.

The plots for ethanol-water and methanol-water mixtures

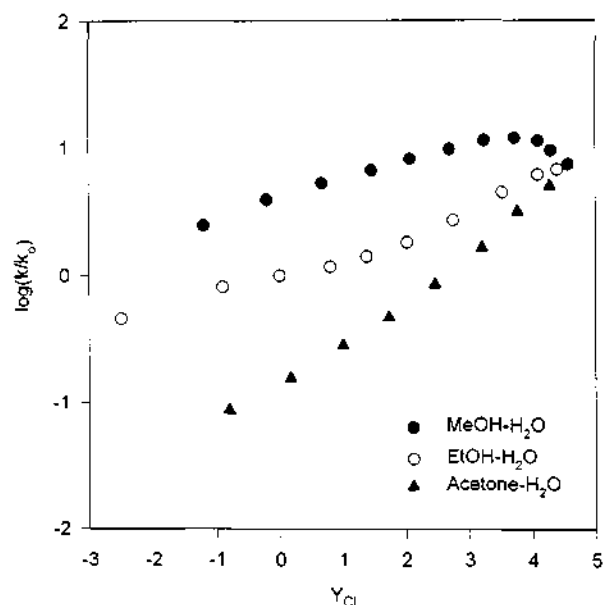


Figure 1. Logarithms of first-order rate constants for solvolyses of phenyl chlorothioformate at 25 °C vs. Y_{Cl} .

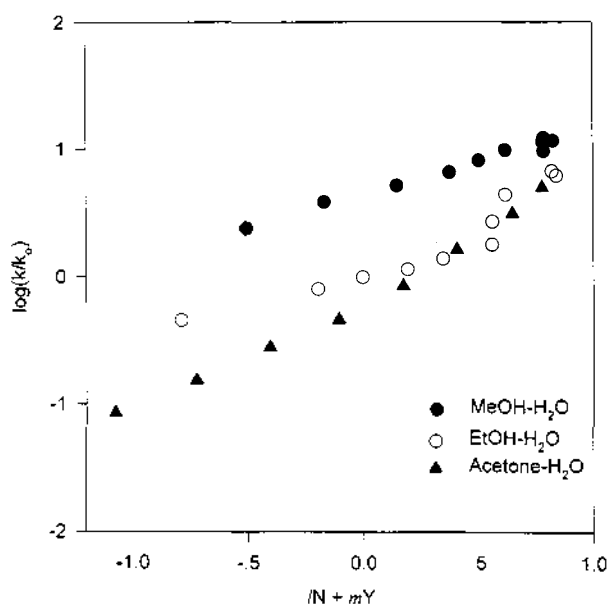


Figure 2. Plot of $\log(k/k_0)$ for phenyl chlorothioformate against $(N+mY)$.

show a very small m value, $m=0.16-0.19$ ($r \geq 0.970$). Such a small m value implies that the solvolysis of phenyl chlorothionoformate in the binary mixtures proceeds by the addition-elimination ($S_{\text{A}}\text{N}$) or associative $S_{\text{N}}2$ mechanism channel rather than by an $S_{\text{N}}1$ channel.

In order to examine the cause of dispersion phenomenon, we correlated the rate data in Table 1 using the extended Grunwald-Winstein equation. The extended Grunwald-Winstein plots still showed dispersions into three separate lines (Figure 2). The nucleophilicity parameter (N) has previously been shown to give a little improvement when an hN term is added to the original Grunwald-Winstein correlations of solvolysis reactions of phenyl chlorothionoformate. Therefore such phenomenon can not be explained as dispersion effect caused by solvent nucleophilicity.

Such phenomenon can be explained as dispersion effect caused by other specific solvent effect or a change of reaction mechanisms according to the variation of solvent composition.⁴ 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 compounds used for determination of Y or Y_{Cl} scale as mentioned above.

In order to examine the cause of this dispersion phenomenon, we correlated the rate data in Table 1 using equations (3) and (4). The plots showed good correlations [$r=0.997$ for eqn.(3) and $r=0.999$ for eqn. (4)] for the solvolysis of phenyl chlorothionoformate (Figures 3 and 4). The aromatic ring parameter (I) has previously been shown to give considerable improvement when an hI term is added to the original Grunwald-Winstein [eqn. (1)] and extended Grunwald-Winstein [eqn. (2)] correlations of the solvolysis reactions of phenyl chlorothionoformate. Therefore, this shows an importance of aromatic ring parameter compared to solvent nucleophilicity for solvolysis of phenyl chlorothionoformate.

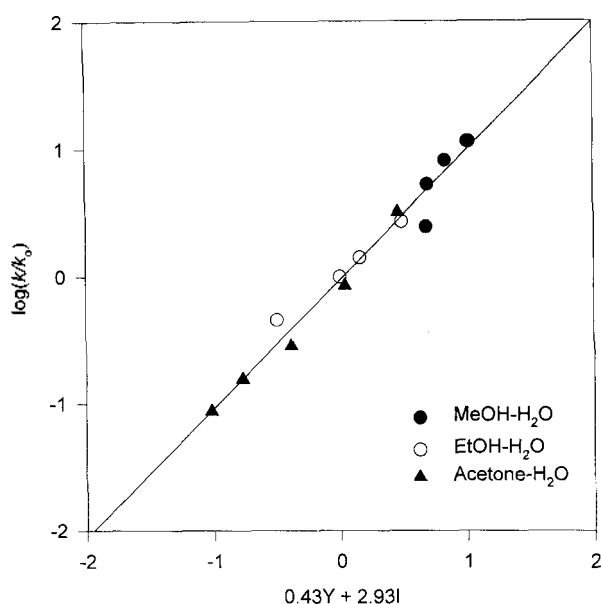


Figure 3. Plot of $\log(k/k_0)$ for phenyl chlorothionoformate against $(0.43Y+2.93I)$.

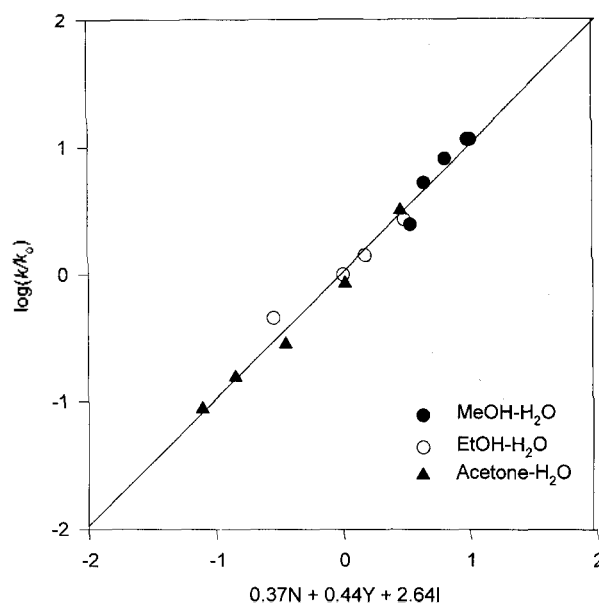


Figure 4. Plot of $\log(k/k_0)$ for phenyl chlorothionoformate against $(0.37N+0.44Y+2.64I)$.

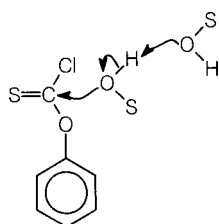
The dispersions in the Grunwald-Winstein correlations in the present studies are caused by the conjugation between the reaction center and the aromatic ring through the phenoxy oxygen atom leading to the large value of sensitivity of I ($h=2.64$) in the full equation (4).

The through conjugation of the ring π system with the nucleophile (solvent in this case) has also been found in the pyridinolysis of phenyl chloroformates.²⁹ In the reaction of phenyl chloroformates with X-pyridines, both the Hammett and Bronsted plots are linear with enhanced substituent constants, ρ_{p} , and basicities, pK_{a} , for strong para π -acceptor X-substituents, $p\text{-CN}$ and $p\text{-CH}_3\text{CO}$. This has been interpreted to indicate the overlap of the electron-rich formate moiety (O-C-O) and the pyridine ring π system in the rate-limiting step. With use of the full equation (4), the l and m values are very similar to the values of 0.37 and 0.44, respectively for the solvolysis of phenyl chlorothionoformate. This study has shown that the magnitude of l and m values associated with a change of solvent composition is able to predict the $S_{\text{N}}2$ transition state.

We have determined the kinetic solvent isotope effect (KSIE), $k_{\text{SOH}}/k_{\text{SOD}}$, for the substrate using deuterated water (D_2O), 50% $\text{D}_2\text{O}\text{-CH}_3\text{OD}$, and methanol- d (CH_3OD), and the results are presented in Table 2. Previous works indicated that the KSIE values are relatively large, ≥ 1.7 , for a general base catalyzed reaction (Scheme 1) but are small, 1.2-1.5, for a $S_{\text{N}}2$ reaction.³⁰ For phenyl chlorothionoformate, the KSIE are 2.02 in methanol, 1.91 in 50% aqueous methanol, and 1.45 in water, the KSIEs are similar for methanol and 50% aqueous methanol. The kinetic solvent isotope effects are consistent with the proposed mechanism of general base catalyzed reaction mechanism. However, the KSIE values (≈ 1.4) for water is smaller than those (≥ 1.9) for 50% aqueous methanol and methanol. These results indicate that the solvolyses of phenyl chlorothionoformate proceed by

Table 2. Rate constants (k , s^{-1}) and kinetic solvent isotope effects for solvolyses of phenyl chlorothionoformate in methanol, 50% methanol and water at 25 °C

v/v %	k_{SOH}	k_{SOD}	KSIE
	$k \times 10^4$		
Water	5.27	3.63	1.45
50% Methanol	6.94	3.63	1.91
Methanol	1.72	0.851	2.02



Scheme 1

predominantly S_N like S_N2 pathway with a relatively tight transition state, where bond formation is more progressed in methanol than in water.

Experimental Section

Methanol, ethanol, acetone were Merck GR grade (<0.1% H_2O), and D_2O and CH_3OD were Aldrich (99.9% D). Distilled water was redistilled with Buchi Fontavapor 210 and treated using ELGA UHQ PS to obtain a specific conductivity of less than 1×10^{-6} mhos/cm. Phenyl chlorothionoformate was Aldrich GR grade (>99.8%). The rates were measured conductometrically at 25 (± 0.03) °C at least in duplicate as described previously,^{31,32} with concentrations of substrate *ca.* 10^{-3} M.

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