

Correlation of the Rates of Solvolysis of Phenyl Chlorodithioformate

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Received July 23, 2002

Solvolytic rate constants at 25 °C are reported for solvolysis of chlorodithioformate (1) in binary mixtures of water with acetone, ethanol, methanol, methanol-d, 50% methanol-d/50% D₂O, and 2,2,2-trifluoroethanol (TFE), and also in TFE-ethanol mixtures. The Grunwald-Winstein plot shows that the three aqueous mixtures exhibit dispersions into separate line. The correlation is improved only slightly by additional parameters N_T for solvent nucleophilicity and/or I for aromatic ring parameter. Rate ratios in solvents of the same Y_{Cl} value, having different nucleophilicity provide measures of the minimum extent of nucleophilic solvent assistance, and the value of 3.35 for $[k_{40EW}/k_{97TFE}]_Y$ (EW = ethanol-water), is consistent with an essentially S_N1 reaction mechanism. This study has shown that the magnitude of l , m and h values associated with a change of solvent composition is able to predict the S_N1 reaction mechanism.

$\log(k/k_o) = mY + lN + hI$

Key Words : Chlorodithioformate, Ionizing power, Nucleophilicity, Solvolysis

Introduction

Dispersion into separate lines in the correlation of the specific rates of solvolysis of a substrate in various binary mixtures was documented¹⁻⁵ in early treatments using the Grunwald-Winstein eqn. (1).⁶⁻⁹

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

In eqn. (1), k is the rate constant for solvolysis in any solvent relative to 80% ethanol-water (k_o), m is the sensitivity of the substrate to the ionizing power (Y) and c is a residual intercept term.

Liu *et al.*, suggested a new ionizing power scale, Y_{BrCl_2} , based on a standard compound [3'-chlorophenyl-2-chloro-adamantane] with an aromatic ring into which the developing charge can delocalize.^{27,29}

In general, dispersion effects in unimolecular solvolysis^{10,11} make smaller contribution to the overall linear free energy relationship (LFER) than solvent nucleophilicity effects in bimolecular solvolysis.^{6,12} It was suggested that a second term which is governed by the sensitivity l to solvent nucleophilicity N_T (Kevill's N_T scale; the solvolysis of S-methyl dibenzothiophenium ion),¹³⁻¹⁵ should be added to Eqn. (1) for bimolecular solvolysis.¹² The resulting Eqn. (2) is often referred to as the extended Grunwald-Winstein equation.¹²

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

Kevill *et al.*, recently suggested¹⁶⁻¹⁹ 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 Eqn. (1) or (2) to give Eqn. (3) or (4), respectively.^{20,21}

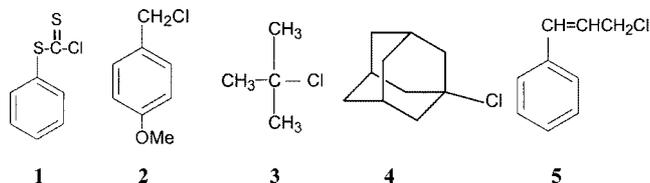
$$\log(k/k_o) = mY + hI + c \quad (3)$$

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

Several other techniques had previously been applied to studies of the solvolysis of and phenyl chloroformate (PhOCOC1), including F/Cl leaving group effects, Hammett treatments of substituent effects, solvent isotope effects, and consideration of the activation parameters.¹⁹ These techniques have all indicated a bimolecular mechanism, almost certainly the addition-elimination (tetrahedral intermediate) type mechanism.¹⁹

In the study of the hydrolysis of phenyl chlorothioformate (PhSCOC1), Queen^{22,23} found that the reaction was slower than the corresponding hydrolysis of phenyl chloroformate and with a positive entropy of activation for hydrolysis of the methyl ester to give strong support to an S_N1 mechanism for the hydrolysis of chlorothioformate ester. However our recent study of the solvolysis of phenyl chlorothioformate (PhOCSC1) has found that the reaction was different results of phenyl chlorothioformate solvolysis reaction.^{19,24} These results indicate that the solvolysis of phenyl chlorothioformate proceed by predominantly S_AN like S_N2 pathway with a relatively tight transition state rather than S_N1 mechanism process.²⁵ We are very interest in mechanisms in solvolysis of phenyl chlorodithioformate (PhSCSC1; **1**) where on replacement of the oxygen atoms of PhOCOC1 with sulfur atoms. Mechanistic changes within the bimolecular pathway could be associated with changes in the stability of the tetrahedral intermediate, with the enforced concerted mechanism lying at one extreme.¹⁹

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In this work, we determined rate constants for solvolysis of **1** in aqueous binary mixtures of acetone, ethanol, methanol, methanol-d and pure water at 25.0 °C, and transition state variation is discussed by applying the Grunwald-Winstein equation, extended Grunwald-Winstein equation, aromatic ring parameter equation, similarity model (Y_{sim}^9) and kinetic solvent isotope effect.

Results

Rate constants for solvolysis of **1** in aqueous binary mixtures of in binary mixtures of water with acetone, ethanol, methanol, methanol-d, 50% methanol-d-50% D₂O, and 2,2,2-trifluoroethanol (TFE)-water (% w/w) and also in TFE-ethanol (% v/v) mixtures at 25.0 °C are reported at Tables 1 and 2.

Table 1. Rate constants (k , s⁻¹) for solvolyses of phenyl chlorodithioformate in aqueous binary mixtures at 25 °C

v/v %	MeOH	EtOH	Acetone
	$k \times 10^3$		
100	0.202	0.0120	
90	0.839	0.0760	
80	3.54	0.389	0.0243
70	11.8	1.51	0.282
60	35.1	4.95	1.57
50	125	18.2	9.51
40	375	80.3	50.3
30	too fast	too fast	233

^aDetermined conductimetrically at least in duplicate; typical error $\pm 3\%$.
^bSolvolyses in MeOD and 50%MeOD-50%D₂O give $k = 0.136(\pm 0.03) \times 10^{-3} \text{ s}^{-1}$ and $87.8(\pm 0.65) \times 10^{-3}$ giving a kinetic solvent isotope effect of 1.49 and 1.42 respectively.

Table 2. Rate constants (k , s⁻¹) for solvolyses of phenyl chlorodithioformate in TFE-H₂O and TFE-EtOH mixtures at 25 °C

w/w %	TFE-H ₂ O	v/v %	TFE-EtOH
	$k \times 10^3$		
100 TFE	6.91	80T-20E	4.03
97 TFE	24.0	60T-40E	0.935
90 TFE	52.5	50T-50E	0.356
70 TFE	153	40T-60E	0.145
50 TFE	254	30T-70E	0.0784
		20T-80E	0.0364

^aDetermined conductimetrically at least in duplicate; typical error $\pm 3\%$.
^b $k_{40\text{EW}}/k_{97\text{TFE}} = 3.35$ ($k_{40\text{EW}}$ taken from Table 1).

Discussion

Kinetic Data. Rate constants (Table 1) increase in the order acetone-H₂O < ethanol-H₂O < methanol-H₂O. The rate increases fast as the water content of the mixtures increase, and it means that the rate is fast accelerated by the solvent with higher ionizing power, Y , suggesting large bond breaking in the transition state. First-order rate constants for solvolysis of **1** vary 3×10^4 fold in alcohol-water mixtures. These results are very similar to those of solvolytic reactions of *p*-methoxybenzoyl chloride,^{2,26,27} cinnamyl chloride (**5**)²⁸ and *p*-methoxybenzyl chloride (**2**).^{26,29}

Reference to Figure 1 shows that the primary substrate **2** is a very good similarity model (Y_{sim}^9) for rate constants for solvolysis of **1**, including TFE-ethanol and TFE-water mixtures.

Rate constants for solvolysis of **2** also correlate well with Y_{BNCl} , but deviation for 100% TFE and other TFE-rich solvent mixtures are noted just as we found with (see Figure 2).²⁹ The result indicate that the rate-determining step for solvolysis of **1** involves extensive bond breaking during formation of transition state. Additional supporting evidence is the similar kinetic solvent isotope effects (KSIE) in methanol (1.22 for **2**,²⁶ 1.11 for **3**,²⁸ and 1.42 for **1**, footnote in Table 1), and 1.42 in 50% methanol-d - 50% D₂O for **1** (footnote in Table 1).

The Grunwald-Winstein plots (eqn. 1) of the rate constants in Tables 1 and 2, presented in Figure 3 using the solvent ionizing power scale Y_{Cl} , based on 1-adamantyl chloride,⁶⁻⁹ show significant dispersion for the three aqueous mixtures, with relatively large slopes for methanol-water ($m = 0.73$, correlation coefficient $r = 0.998$), ethanol-water ($m = 0.74$, $r = 0.994$) and acetone-water ($m = 0.99$, $r = 0.999$). Also the

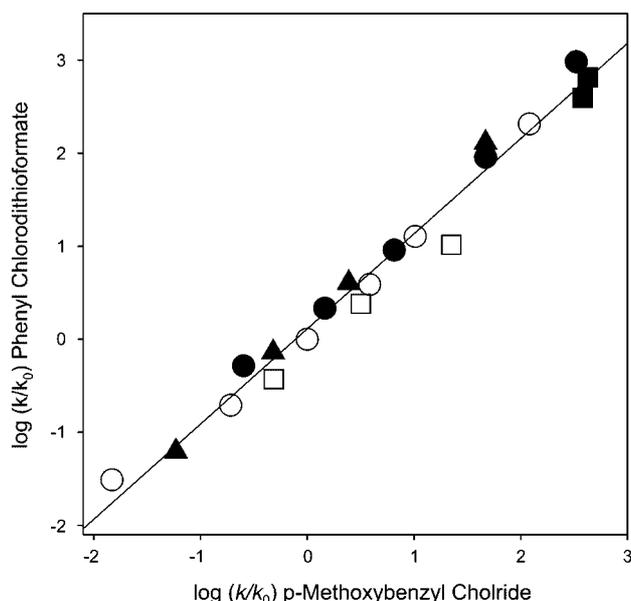


Figure 1. Logarithms of rate constants for solvolyses of phenyl chlorodithioformate versus solvolyses of *p*-methoxybenzyl chloride at 25 °C (slope = 1.02, $r = 0.989$, solvent code ●, methanol; ○, ethanol; ▲, acetone; ■, TFE-H₂O; □, TFE-EtOH).

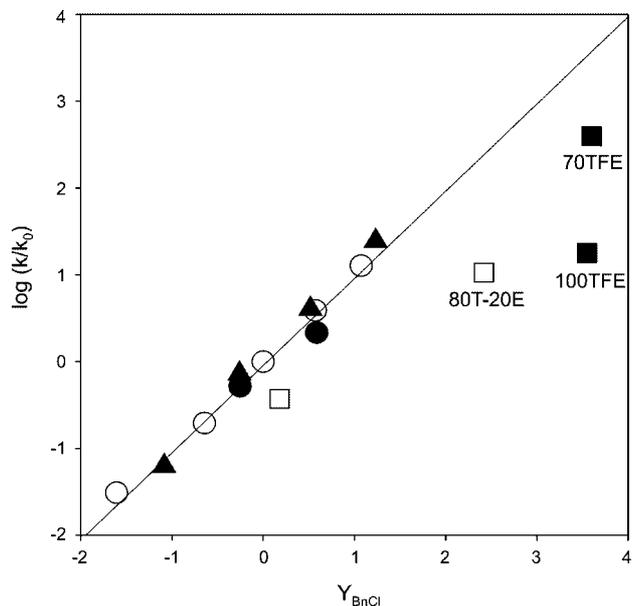


Figure 2. Logarithms of first-order rate constants for solvolyses of phenyl chlorodithioformate at 25 °C $\log(k/k_0)$ vs. Y_{BnCl} (solvent code ●, methanol; ○, ethanol; ▲, acetone; ■, TFE-H₂O; □, TFE-EtOH).

data points for TFE-water and TFE-ethanol show no major deviations from the Grunwald-Winstein correlations (Figure 3).

The low nucleophilicity provide measures of the minimum extent of nucleophilic solvent assistance (*e.g.*, $[k_{40EW}/k_{97TFE}]_Y = 3.35$, EW = ethanol-water).³⁰ The low nucleophilicity and high ionizing power of the fluorinated alcohol, CF₃CH₂OH, show small deviation from Figure 1. Such a large m value and small value of k_{40EW}/k_{97TFE} imply that the solvolysis of **1**

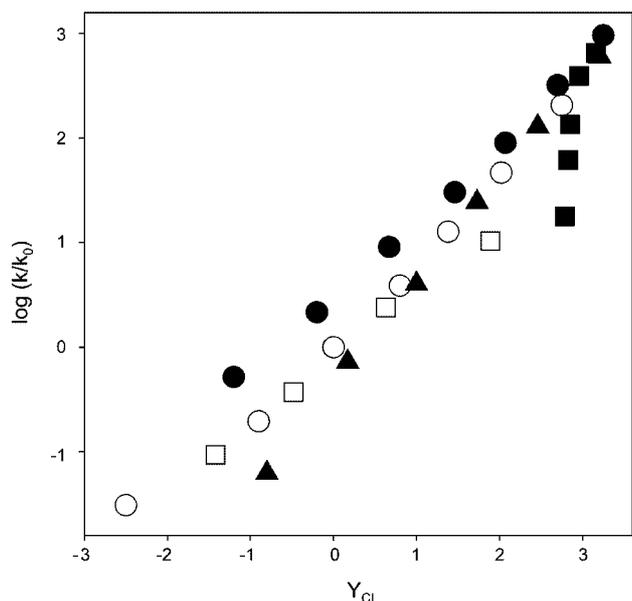


Figure 3. Logarithms of first-order rate constants for solvolyses of phenyl chlorodithioformate at 25 °C $\log(k/k_0)$ vs. Y_{Cl} (solvent code ●, methanol; ○, ethanol; ▲, acetone; ■, TFE-H₂O; □, TFE-EtOH).

in the binary mixtures proceeds by the S_N1 pathways channel rather than by an pure S_N2 reaction channel.

In order to examine the cause of this dispersion phenomenon, we correlated the rate data in Table 1 using eqn. (2). The nucleophilicity parameter (N_T) have been shown to give a fairly good correlation when an lN_T term are added to the original Grunwald-Winstein [eqn. (1)] correlations of the solvolysis of **1** (see Figure 4). However, the ring parameter (l) have been shown to give considerable improvement when an hl term are added to the extended Grunwald-Winstein [eqn. (2)] correlations of the solvolysis of **1** (see Figure 5). This shows the importance of solvent nucleophilicity parameter as well as the aromatic ring parameter for solvolysis of **1**. Therefore such phenomenon can be explained as dispersion effect caused by solvent nucleophilicity parameter and aromatic ring effect. The dispersions in the Grunwald-Winstein correlations in the present studies are caused by the conjugation between the reaction center and aromatic ring through the sulfur atom leading the medium value of sensitivity of l ($h = 0.71 \pm 0.299$) in the full eqn. (4). The conjugation of the ring π system with the reaction center carbon is also conceivable in the solvolysis of phenyl chlorothionoformate²⁴ as in the solvolysis of cinnamyl chloride pyridinolysis of phenyl chloroformates.³¹ This result has been interpreted to indicate the positive charge is delocalized partially into the aromatic ring π system through lone pair electron of sulfur atom in the rate-limiting step. With use of the full equation (4), the l and m values are similar to the values of 0.44 ± 0.109 and 1.01 ± 0.067 for the solvolysis of **1**. These l and m values are very similar to those obtained for solvolysis of *tert*-butyl chloride,³² cinnamyl chloride²⁸ and 1-adamantyl chloride (correlation coefficient of 0.977),³³ which are believed to proceed by S_N1 pathway. However, in case of solvolysis of 1-adamantyl

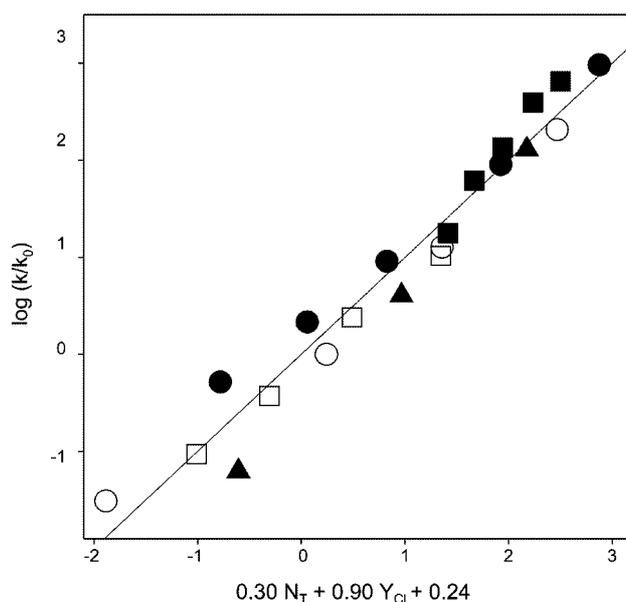


Figure 4. Plot of $\log(k/k_0)$ for phenyl chlorodithioformate against $(0.34 N_T + 0.90 Y_{Cl} + 0.24)$ $r = 0.978$ (solvent code ●, methanol; ○, ethanol; ▲, acetone; ■, TFE-H₂O; □, TFE-EtOH).

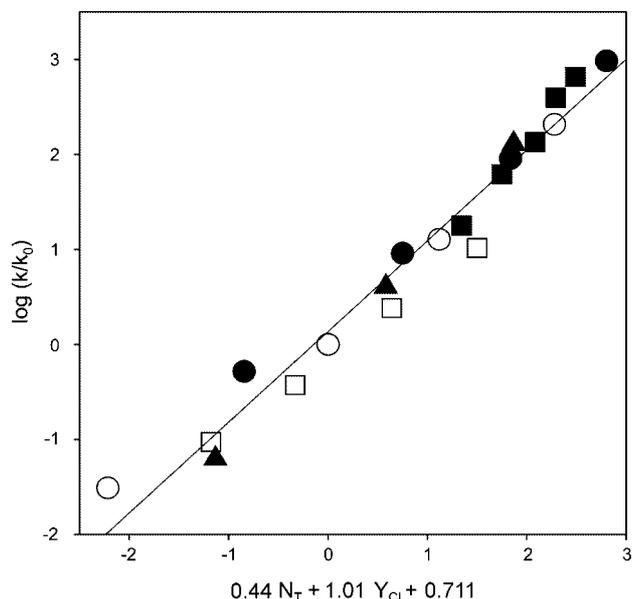


Figure 5. Plot of $\log(k/k_0)$ for phenyl chlorodithioformate against $(0.44 N_T + 1.01 Y_{Cl} + 0.71 I)$. $r = 0.979$ (solvent code \bullet , methanol; \circ , ethanol; \blacktriangle , acetone; \blacksquare , TFE-H₂O; \square , TFE-EtOH).

chloride, the l value is very small (0.14) value, because of the relatively rigid and caged structure of the adamantyl skeleton, rear-side nucleophilic attack on covalent substrate is inhibited sterically.³³ The solvolysis of **1** follow an ionization mechanism (S_N1 mechanism), with a considerable solvation of the developing carbocation.

The specific rates (Table 2) of solvolysis of **1** in the four aqueous trifluoroethanol and five ethanol-trifluoroethanol solvents have also been correlated using extended Grunwald-Winstein equation (see Figure 6). The values obtained are 1.06 ± 0.078 for m , 0.49 ± 0.10 for l , and 0.27 ± 0.123 for c with the correlation coefficient of 0.991. This study has shown that the magnitude of l and m values associated with a change of solvent composition can be used to predict the ionization mechanism (S_N1) rather than by an S_N2 mechanism channel.

Third Order Reaction Model. For solvolysis in water-cosolvent mixtures, interpretation based on a third order mechanism is more complex, but significant new information is available because cosolvent is acting as a general base

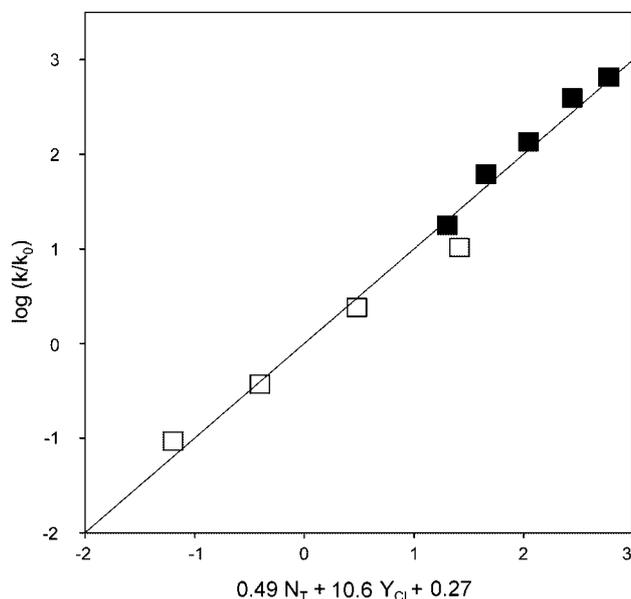


Figure 6. Plot of $\log(k/k_0)$ for phenylchlorodithioformate against $(0.49 N_T + 10.6 Y_{Cl} + 0.27)$ $r = 0.991$ (solvent code \blacksquare , TFE-H₂O; \square , TFE-EtOH).

catalyst. Thus, there are two possible third-order rate constants in the solvolysis reaction: (i) k_{ww} for a mechanism in which one molecule of water act as a nucleophile and second molecule of water act as a general base; (ii) k_{wc} in which water act as a nucleophile and cosolvent act as a general base.³⁴ Therefore observed first-order rate constants in water-acetone mixtures are given by Eqn. (7).^{23,34}

$$k_{\text{obs}} = k_{\text{ww}}[\text{water}]^2 + k_{\text{wa}}[\text{water}][\text{acetone}] \quad (7)$$

The third-order rate constant k_{wa} can be obtained by the plot of $k_{\text{obs}}/[\text{H}_2\text{O}]_2$ versus $[\text{acetone}]/[\text{H}_2\text{O}]$ (Eqn. 8).

$$k_{\text{obs}}/[\text{H}_2\text{O}]_2 = k_{\text{ww}} + k_{\text{wa}} [\text{acetone}]/[\text{H}_2\text{O}] \quad (8)$$

This type of plot showed a straight line of positive slope for the reactions proceeding with an S_N2 mechanism (e.g. solvolysis of *p*-nitrophenyl chloroformate).³⁴ The plot for the solvolysis of chlorodithioformate, however, leads to an exponential decay curve shown in Figure 7. This means that the rate is independent of the catalysis, i.e., k_{wa} is non-existent and the rate dependent on solely on the ionizing

Table 3. Correlation analyses against different Y , N , I and Y_{sim}

Compound	Parameters	n	r	$m(\text{s.d.})^a$	$l(\text{s.d.})^a$	$h(\text{s.d.})^a$	$c(\text{s.d.})^a$
1	Y_{Cl}	29	0.961	0.77(0.042)			
	Y_{Cl}, N_T	21	0.978	0.90(0.054)	0.34(0.081)		0.24(0.084)
	$Y_{Cl}, N_{T(\text{TFE})}$	9	0.991	1.06(0.078)	0.49(0.100)		0.27(0.123)
	Y_{Cl}, N_T, I	20	0.979	1.01(0.067)	0.44(0.109)	0.71(0.299)	
	Y_{sim}^b	20	0.979	1.02(0.035)			0.11(0.050)
3 ^c	Y_{Cl}, N_T		0.977	0.83(0.080)	0.37(0.090)		
4 ^d	Y_{Cl}, N_T	11	0.999	0.87(0.017)	0.14(0.028)		-0.09(0.030)
5 ^e	Y_{Cl}, N_T, I	24	0.988	0.88(0.041)	0.23(0.073)	0.23(0.073)	

^aStandard deviation. ^b $\log(k/k_0)$ for *p*-methoxybenzyl chloride (2); data from refs. 26 and 28. ^c $\log(k/k_0)$ for *tert*-butyl chloride (3); data from refs. 8 and 32. ^d $\log(k/k_0)$ for 1-adamantyl chloride (4); data from refs. 3 and 33. ^e $\log(k/k_0)$ for cinnamyl chloride (5); data from refs. 28.

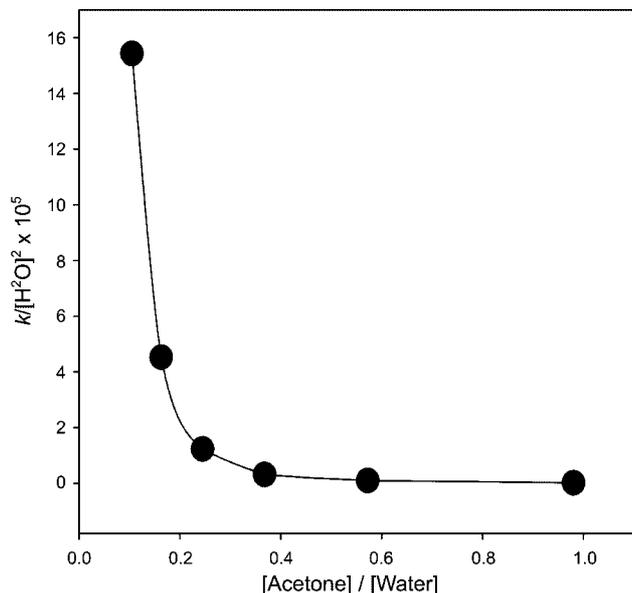


Figure 7. Plot of third-order rate constant versus [Acetone]/[Water].

power of the solvent, Y . In fact the plot of $\log k$ (third order) against volume percentage acetone shows a straight line of negative slope, which is exactly similar to that of $\log k$ versus Y plot. We therefore conclude that the rate is solely dependent on Y (as required for an S_N1 reaction) and there is no catalysis by solvent molecule.

We try to further investigate of a third order model^{34,35} based on an electrophilic catalyst by one molecule of solvent in TFE-ethanol mixtures. For solvolysis in TFE-ethanol binary mixtures, there are four possible third order rate constants: (i) k_{EE} ; one molecule of ethanol acting as a nucleophile and second molecule of ethanol acting as an electrophilic catalyst. (ii) k_{ET} ; one molecule of ethanol acting

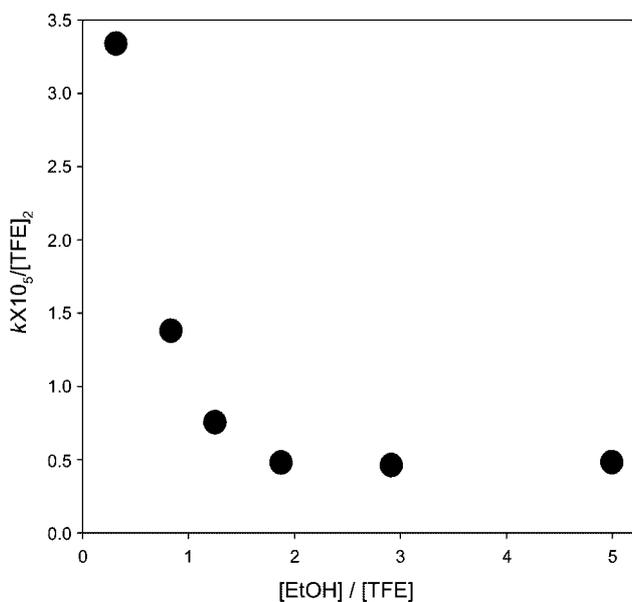
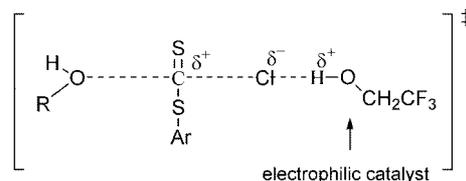


Figure 8. Plot of third-order rate constant versus [EtOH]/[TFE].



Scheme 1

as a nucleophile and a second molecule of TFE acting as an electrophilic catalyst. (iii) k_{TE} ; the case of the contrast role to the k_{ET} term. (iv) k_{TT} ; the role of a molecule of TFE solvent as a nucleophile and an electrophilic catalyst.

But considering the low nucleophilic character of TFE solvent (the lower nucleophilicity of TFE, $N_T = -0.41$ relative to ethanol, $N_T = 0.06$),¹³⁻¹⁵ the k_{TT} and k_{TE} terms may be ignored. Consequently, we obtain eqn. (9) with possible third order terms.

$$k_{\text{obs}} = k_{EE}[\text{ethanol}]^2 + k_{ET}[\text{ethanol}][\text{TFE}] \quad (9)$$

These can be rearranged to make a useful linear form eqn. (10)

$$k_{\text{obs}}/[\text{ethanol}]^2 = k_{EE} + k_{ET}[\text{TFE}]/[\text{ethanol}] \quad (10)$$

If the rate constants are not variable, or vary in the same way with solvent, then a plot of $k_{\text{obs}}/[\text{ethanol}]^2$ vs $[\text{TFE}]/[\text{ethanol}]$ should give a straight line. However, the plots are not straight lines but exponential type curves, as shown in Figure 8. This means that the rate is dependent on the electrophilic catalysis by trifluoroethanol, *i.e.*, the third order rate is dominantly influenced by the ionizing power of the solvent, Y as increasing trifluoroethanol concentration increases. In fact the plot of $\log k$ (third order) against volume percentage of trifluoroethanol shows a straight line with a positive slope, which is exactly similar to that of $\log k$ versus Y plot. We therefore conclude that the rate is solely dependent on Y (as required for an S_N1 reaction) and there is electrophilic catalysis by trifluoroethanol solvent molecule (Scheme 1).

Conclusions

Solvolysis of chlorodithioformate (**1**) responds almost identically to those of *p*-methoxybenzyl chloride (**2**) and cinnamyl chloride (**5**) to changes in solvent ionizing power and solvent nucleophilicity. The rates of solvolysis of *p*-methoxybenzyl chloride also respond to solvent changes very similarly. Consequently, it may be deduced that all four substrates solvolysis by very similar rate-determining steps. Thus solvolysis of **1** can be concluded to proceed by an ionization mechanism (S_N1 mechanism) with a considerable solvation of the developing carbocation. This study has shown that the magnitude of l , m and $[k_{40EW}/k_{97TFE}]_Y$ values associated with a change of solvent composition is able to predict the ionization mechanism (S_N1) rather than by an S_N2 mechanism channel.

Experimental Section

Material and Rate measurements. Methanol, ethanol, and acetone were Merck GR grade (< 0.1% H₂O), and distilled water was redistilled with Buchi Fontavapor 210 and treated using ELGA UHQ PS to obtain specific conductivity of less than 1×10^{-6} mhos/cm. Chlorodithioformate (Aldrich GR grade, 99%) was used without further purification.

The rates were measured conductometrically at 25 (± 0.03)°C at least in duplicate as described previously,^{1,25,36} with concentrations of substrate *ca.* 10^{-3} M.

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