Correlation of the Rates of Solvolysis of Phenyl Chlorodithioformate

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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 N1 for solvent nucleophilicity and/or I for aromatic ring parameter. Rate ratios in solvents of the same YCI value, having different nucleophilicity provide measures of the minimum extent of nucleophilic solvent assistance, and the value of 3.35 for [kHOCICl/kTFE]l (EW = ethanol-water), is consistent with an essentially S1 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 S1/S2 reaction mechanism.

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 documented in early treatments using the Grunwald-Winstein eqn. (1).6,9

\[ \log(k/k_o) = mY + c \] (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, \( Y_{BnCl2} \), based on a standard compound \( [3'- chlorophenyl-2-chloroadamantane] \) with an aromatic ring into which the developing charge can delocalize.27,29

In general, dispersion effects in unimolecular solvolysis10,11 make smaller contribution to the overall linear free energy relationship (LFER) than solvent nucleophilicity effects in bimolecular solvolysis.5,12 It was suggested that a second term which is governed by the sensitivity I to solvent nucleophilicity \( N_I \) (Kevill’s NT scale; the solvolysis of S-methyl dibenzo thiophenium 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

\[ \log(k/k_o) = mY + lN_I + c \] (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

\[ \log(k/k_o) = mY + hI + c \] (3)
\[ \log(k/k_o) = mY + lN_I + hI + c \] (4)

Several other techniques had previously been applied to studies of the solvolysis of phenyl chloroformate (PhOCOCI), 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 (PhScOCI), Queen2,23 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 S1 mechanism for the hydrolysis of chlorothioformate ester. However our recent study of the solvolysis of phenyl chlorothionoformate (PhOCSCI) has found that the reaction was different results of phenyl chlorothioformate solvolysis reaction.19,24 These results indicate that the solvolysis of phenyl chlorothionoformate proceed by predominantly S1N like S1/2 pathway with a relatively tight transition state rather than S1 mechanism process.25 We are very interest in mechanisms in solvolysis of phenyl chlorodithioformate (PhSDCl; 1) where on replacement of the oxygen atoms of PhOCOCI 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 ($Y_{sim}$) 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

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

* Determined conductimetrically at least in duplicate; typical error ± 3%.

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

<table>
<thead>
<tr>
<th>TFE-H2O</th>
<th>TFE-EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k \times 10^3$</td>
<td>$k \times 10^3$</td>
</tr>
<tr>
<td>w/w %</td>
<td>v/v %</td>
</tr>
<tr>
<td>100 TFE</td>
<td>6.91</td>
</tr>
<tr>
<td>97 TFE</td>
<td>24.0</td>
</tr>
<tr>
<td>90 TFE</td>
<td>52.5</td>
</tr>
<tr>
<td>70 TFE</td>
<td>153</td>
</tr>
<tr>
<td>50 TFE</td>
<td>254</td>
</tr>
<tr>
<td></td>
<td>20T-80E</td>
</tr>
</tbody>
</table>

* Determined conductimetrically at least in duplicate; typical error ± 3%.

**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 ($Y_{sim}$) 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 3,23 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 ($m = 0.99$, correlation coefficient $r = 0.999$), ethanol-water ($m = 0.74$, $r = 0.994$) and acetone-water ($m = 0.99$, $r = 0.999$). Also the
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., \(k_{30EW}/k_{97TFE}\)) 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 \((I)\) have been shown to give considerable improvement when an \(hI\) 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 \(I\) (\(h = 0.71 \pm 0.299\)) in the full eqn. (4). The conjugation of the ring \(\pi\) system with the reaction center carbon is also conceivable in the solvolysis of phenyl chlorothionoformate\(^{24}\) as in the solvolysis of cinnamyl chloride pyridinolsis of phenyl chloroformates.\(^{31}\) This result has been interpreted to indicate the positive charge is delocalized partially into the aromatic ring \(\pi\) 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 \(\pm\) 0.109 and 1.01 \(\pm\) 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 chloride\(^{28}\) 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...
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\( _N \)\( _1 \) 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 \( 1.06 \pm 0.078 \) for \( m \), \( 0.49 \pm 0.10 \) for \( l \), and \( 0.27 \pm 0.123 \) 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 to predict the ionization mechanism (S\( _N \)\( _1 \)) rather than by an S\( _N \)\( _2 \) mechanism.

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. 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).\(^{23,34} \)

\[
\frac{k_{obs}}{[H_2O]^2} = k_{ww}[water]^2 + k_{wc}[water][acetone]
\]

The third-order rate constant \( k_{wc} \) can be obtained by the plot of \( k_{obs}/[H_2O]^2 \) versus [acetone]/[H\( _2 \)O] (Eqn. 8).

\[
k_{obs}/[H_2O]^2 = k_{ww} + k_{wc} [acetone]/[H_2O]
\]

This type of plot showed a straight line of positive slope for the reactions proceeding with an S\( _N \)\( _2 \) 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., \( k_{ww} \) is non-existent and the rate dependent on solely on the ionizing catalyst.

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

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

\(^a\)Standard deviation. \(^b\)log \((k/k_o)\) for \( p \)-methoxybenzyl chloride (2); data from refs. 26 and 28. \(^c\)log \((k/k_o)\) for tert-butyl chloride (3); data from refs. 8 and 32. \(^d\)log \((k/k_o)\) for 1-adamantyl chloride (4); data from refs. 3 and 33. \(^e\)log \((k/k_o)\) for cinnamyl chloride (5); data from refs. 28.
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 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 a electrophilic catalyst. (ii) \( k_{ET} \): one molecule of ethanol acting as a nucleophile and a second molecule of TFE acting as 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 a electrophilic catalyst.

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

\[
k_{obs} = k_{EE} [\text{ethanol}]^2 + k_{ET} [\text{ethanol}][\text{TFE}] \tag{9}
\]

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

\[
k_{obs}/[\text{ethanol}]^2 = k_{EE} + k_{ET}[\text{TFE}]/[\text{ethanol}] \tag{10}
\]

If the rate constants are not variable, or vary in the same way with solvent, then a plot of \( k_{obs}/[\text{ethanol}]^2 \) vs \([\text{TFE}]/[\text{ethanol}]\) should give a straight line. However the plots are not straight line but exponential type curve, as shown in Figure 8. This means that the rate is dependent of the electrophilic catalysis by trifluoroethanol, \( i.e. \), the third order rate is dominantly influenced by the ionizing power of the solvent, \( Y \) as increasing of trifluoroethanol concentration increases. In fact the plot of \( \log k \) (third order) against volume percentage of trifluoroethanol shows a straight line with 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) respond 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 \( p \)-methoxybenzoyl 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 \( [k_{ET}/k_{EE}]_P \) 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.¹²⁵ ¹²⁶

with concentrations of substrate ca. 10⁻³ M.

References