Understanding Solvent Effects in the Solvolyses of 4-Fluorophenyl Chlorothionoformate

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Abstract

The solvolyses of 4-fluorophenyl chlorothionoformate (**1**) are studied in fifteen binary aqueous organic mixtures of widely varying nucleophilicity and ionizing power values. The specific rates of solvolyses of **1** are plotted against the specific rates of solvolysis observed for phenyl chloroformate (**2**) and deviations from the line-of-best-fit are observed in some of the highly ionizing aqueous fluoroalcohol mixtures. An analysis of the solvolytic data accumulated using the extended (two-term) Grunwald-Winstein equation confirms this deviant behavior and shows that dual bimolecular addition-elimination and unimolecular ionization channels occur in the solvolyses of **1**.

Keywords: Solvolysis; Grunwald-Winstein equations; nucleophilic solvation; chlorothionoformate.

1. Introduction

Compounds such as 4-fluorophenyl chlorothionoformate (**1**) that contain fluorophenyl groups are important in asymmetric synthesis in medicinal chemistry, as fluorine substitution in a drug molecule can alter the pharmacodynamic activity and toxicity of biologically active drug molecules [1]. Chlorothionofomate esters in general are also employed as useful reagents for the preparation of thiocarbonate esters, nitriles, and isonitriles [2,3].

As a result a number of research groups [4-19] are now involved in the investigation of the hydrolysis, aminolysis and alcoholysis of alkyl and aryl chlorothionoformates. Queen [4], in an analysis of the hydrolysis of a series of alkyl chlorothionoformates together with their activation parameters and solvent isotope effects, concluded that these compounds hydrolyze by S_N1 mechanisms. Lee et al. [5,6,13] favored a concerted process with a general base catalyzed S_N2 transition state for the solvolysis of alkyl and aryl chlorothionoformates, and a concerted mechanism [15] with a four-membered hydrogen bonded cyclic transition state for the aminolysis of aryl chlorothionoformates with anilines in acetonitrile. Castro, Santos and coworkers [7,8,11,14,16,17] proposed that the aminolysis of chlorothionoformates is a stepwise process with the formation of a zwitter ionic intermediate while the phenolysis is concerted.

We favor the use [19] of the extended Grunwald-Winstein equation (equation 1) [20] for solvolytic studies and have proposed that side-by-side addition-elimination ($A_N + D_N$) and S_N1 ionization ($D_N + A_N$) mechanisms often occur during the solvolysis of chloro- (ROCOCl), chlorothio- (RSCOCl), chlorothiono- (ROCSCl), and chlorodithioformate esters (RSCSCl) [10,18,19,21,22].

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

In equation 1, k and k_o are the specific rates of solvolysis of a substrate in a given solvent and the standard solvent (80% ethanol) respectively, l is the sensitivity to changes in solvent nucleophilicity (N), m represents the sensitivity that controls the importance of the solvent ionizing power value (Y). N_T scales [23] based on the solvolyses of the *S*-methyldibenzothiophenium ion and Y_X values based on the solvolyses of 1- and 2-adamantyl

derivatives [24] have become the recognized standards for considerations of the Grunwald-Winstein linear free energy relationship (LFER).

Based on results obtained through Grunwald-Winstein (equation 1) analyses, we recently recommended [19] that the *l* (1.66) and *m* (0.56) values obtained for solvolyses of phenyl chloroformate (**2**), and the *l* = 0.69, *m* = 0.95 values obtained for phenyl chlorodithioformate (**3**), be taken as appropriate standards for the bimolecular addition-elimination ($A_N + D_N$) and unimolecular S_N1 ionization ($D_N + A_N$) pathways respectively. The *l* value of 0.69 seen in the chlorodithioformate ester was said to represent a strong rear-side nucleophilic solvation of the developing thioacylium cation [19].

We also pointed out [19] that in RXCXCl (X = O or S) substrates superimposed mechanisms were observed and the ranges of dominance for each was dependent on the R group, if X = O or S, the solvent nucleophilicity value, and the solvent ionizing power value.

Lee [25] analyzing CNDO/2 studies on conformation and reactivity suggested that the most stable geometries for RXCXCl (where X = S or O) involve a configuration where the C=O or the C=S is *syn* with respect to R. Bentley and others [26] confirmed this conformation and in Figure 1, the molecular structures for 4-fluorophenyl chlorothionoformate (**1**), phenyl chloroformate (**2**), phenyl chlorodithioformate (**3**), phenyl chlorothioformate (**4**), phenyl chlorothionoformate (**5**), and phenyl fluorothionoformate (**6**) are shown where the halogen atom is in a *trans* position with respect to the aryl group i.e. the structures are drawn in a *syn* conformation.

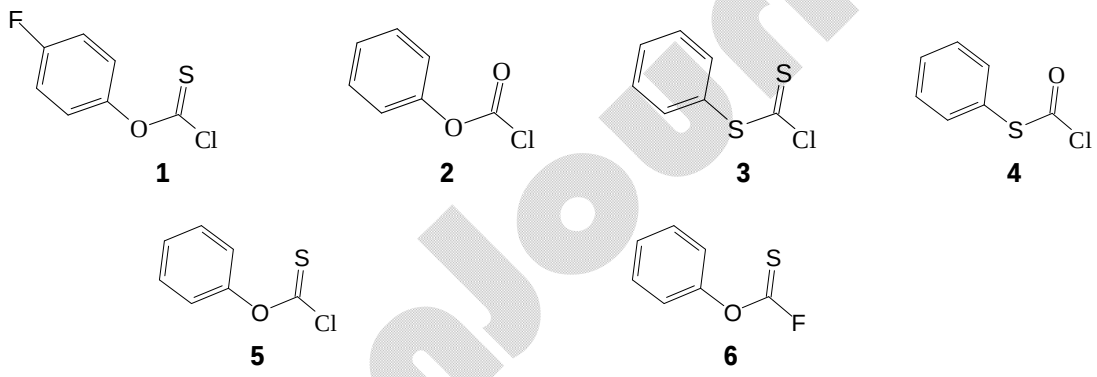


Figure 1: Molecular structures of 4-fluorophenyl chlorothionoformate (**1**), phenyl chloroformate (**2**), phenyl chlorodithioformate (**3**), phenyl chlorothioformate (**4**), phenyl chlorothionoformate (**5**) and phenyl fluorothionoformate (**6**).

Kyong, and Kevill et al. [27] have recently showed that phenyl fluorothionoformate (**6**) has an *l*/*m* ratio of 3.38, a solvent deuterium isotope effect value for methanolysis (k_{MeOH}/k_{MeOD}) of 2.11, and entropy of activation range of -26.2 to -21.0 cal $mol^{-1}K^{-1}$. This data strongly indicated that **6** solvolyzes by a bimolecular pathway in all solvents studied with the addition step of the addition-elimination ($A_N + D_N$) reaction being rate-determining [27].

In the present paper, we have reported the first-order specific rate constants at 35.0°C for the solvolyses of **1** in ethanol and methanol and thirteen binary mixtures of aqueous ethanol (EtOH), aqueous methanol (MeOH), aqueous acetone, aqueous 2,2,2-trifluoroethanol (TFE), and aqueous 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Applying the concept of a similarity model [28] we compare the specific rates of solvolysis of **1** against those of **2**, examine the solvent-deviations from the goodness-of-fit line, and justify the results obtained by employing correlation analyses using the two-term Grunwald-Winstein LFER (equation 1).

2. Methods

The 4-fluorophenyl chlorothionoformate (96%, TCI America) was used as received. Solvents were purified and the kinetic runs carried out as described previously [19]. A substrate concentration of approximately 0.005 M

in a variety of solvents was employed. For some of the runs, calculation of the specific rates of solvolysis (first-order rate coefficients) was carried out by a process [19] in which the conventional Guggenheim treatment was modified so as to give an estimate of the infinity titer, which was then used to calculate for each run a series of integrated rate coefficients. The specific rates and associated standard deviations, as presented in Table 1, were obtained by averaging all of the values from, at least, duplicate runs.

Multiple regression analyses were carried out using the Excel 2007 package from the Microsoft Corporation, and the SigmaPlot 9.0 software version from Systat Software, Inc., San Jose, CA, was used for the Guggenheim treatments.

3. Results and Discussion

The first-order specific rates of solvolysis of **1** at 35.0 °C in fifteen pure and aqueous organic mixtures are reported in Table 1. The specific rates of **1** increase as the amount of water in the binary aqueous mixture increases. A small gradual increase in rate coefficients is also observed in the highly ionizing fluoroalcohols indicating that in these solvents, there is some nucleophilic participation of the solvent in the transition state.

Table 1: Specific rates of solvolysis (*k*) of **1**, in several binary solvents at 35.0 °C and literature values for N_T and Y_{Cl}.

Solvent (%)[a]	1 @ 35.0 °C; $10^5 k$, s^{-1}[b]	N_T[c]	Y_{Cl}[d]
100% MeOH	55.3 ± 1.3	0.17	-1.2
90% MeOH	86.0 ± 1.3	-0.01	-0.20
80% MeOH	116 ± 6	-0.06	0.67
100% EtOH	20.0 ± 1.0	0.37	-2.50
90% EtOH	24.8 ± 0.5	0.16	-0.90
80% EtOH	28.2 ± 1.8	0.00	0.00
80% Acetone	3.44 ± 0.06	-0.35	-2.39
97% TFE (w/w)	0.467 ± 0.020	-3.30	2.83
90% TFE (w/w)	0.600 ± 0.010	-2.55	2.85
70% TFE (w/w)	2.08 ± 0.13	-1.98	2.96
80T-20E	0.272 ± 0.010	-1.76	1.89
50T-50E	3.21 ± 0.14	-0.64	0.60
97%HFIP (w/w)	3.43 ± 0.09	-5.26	5.17
90%HFIP (w/w)	4.18 ± 0.08	-3.84	4.41
70%HFIP (w/w)	5.49 ± 0.07	-2.94	3.83

[a] Substrate concentration of *ca.* 0.0052 M; binary solvents on a volume-volume basis at 25.0 °C, except for TFE-H_2O and HFIP-H_2O solvents which are on a weight-weight basis. T-E are TFE-ethanol mixtures. [b] With associated standard deviation. [c] Refs. 19,23. [d] Refs. 19,24.

A plot of log $(k/k_o)_1$ versus log $(k/k_o)_2$ shown in Figure 2, exhibits considerable deviations for some of the aqueous fluoroalcohol mixtures. Indeed this plot results in a very poor correlation coefficient (*R*) of 0.720, slope of 0.33 ± 0.09, intercept (*c*) of -0.16 ± 0.20, and *F*-test of 14.

Using all of the fifteen specific rates of solvolysis of **1** listed in Table 1 within the extended Grunwald-Winstein equation (equation 1) leads to a very poor correlation with a correlation coefficient (*R*) of 0.627, *l* =0.43 ± 0.33, *m* = 0.11 ± 0.25, *c* = -0.17 ± 0.27, and a very low *F*-test value of 4. This substandard correlation result expresses the possibility of the presence of dual mechanisms in the solvolyses of **1**.

A careful observation of Figure 2 indicates that 97%, 90%, and70% HFIP, and 97% and 90% TFE deviate significantly from the line of best fit. Removal of these five highly ionizing solvents for a correlation analysis of **1** against **2**, results in a significantly improved correlation coefficient (R) of 0.994, slope of 0.92 ± 0.04, *c* = 0.08 ± 0.04, and an *F*-test value of 622. This exceptional correlation suggests that the mechanism of **1** in the remaining ten more nucleophilic solvents is exactly the same as that proposed for **2**. The slope of 0.92

observed in the plot of log $(k/k_o)_1$ versus log $(k/k_o)_2$ in these ten solvents, is consistent with the proposal of a slightly earlier transition state for the solvolyses of **1** when compared to that seen for the solvolyses of **2**.

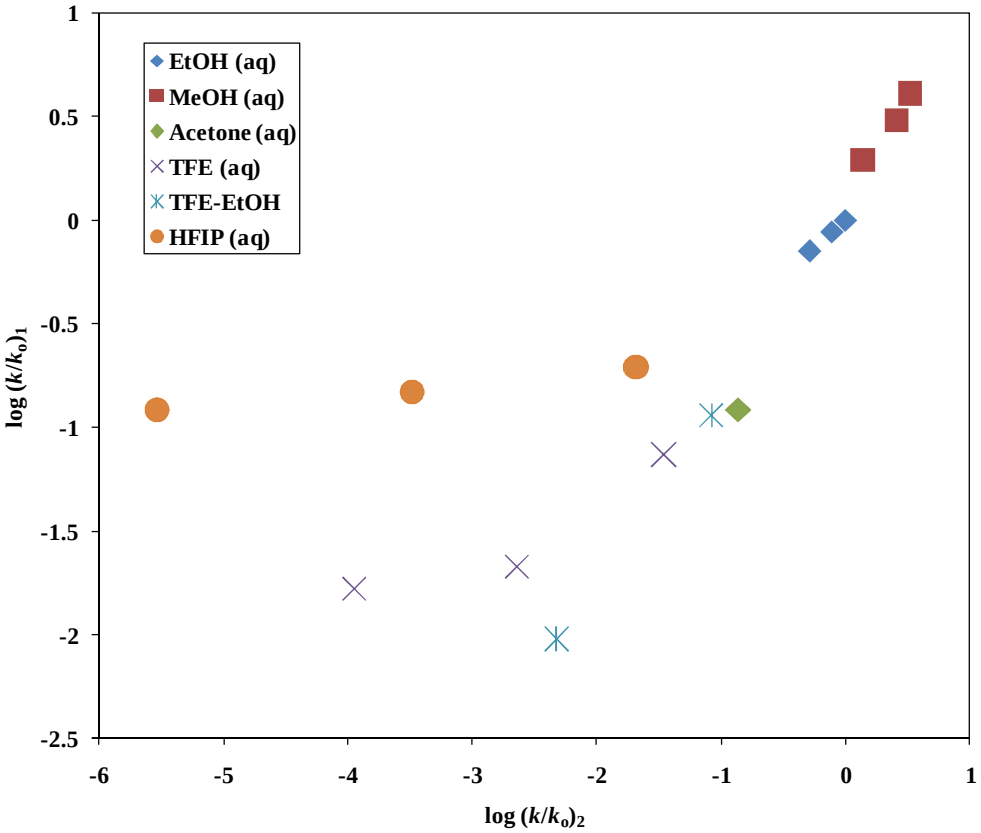


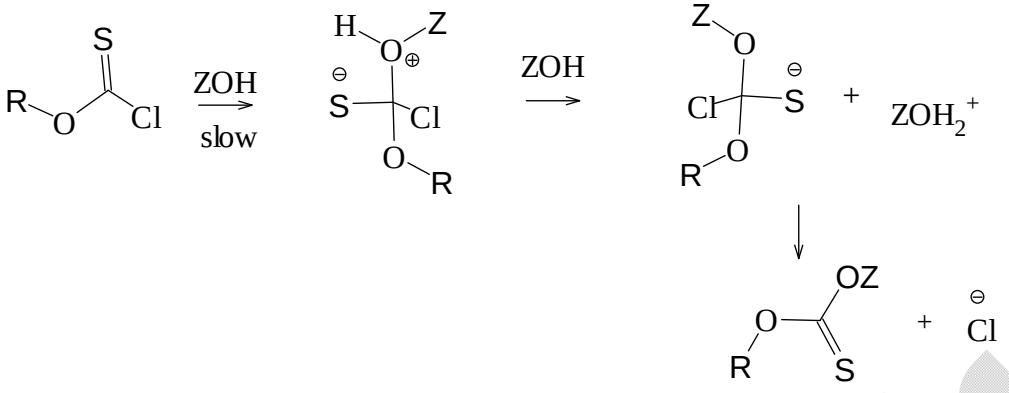
Figure 2: The plot of log (k/k_o) for 4-fluorophenyl chlorothionoformate (**1**) against log (k/k_o) for phenyl chloroformate (**2**) in the fifteen common pure and binary solvents studied.

In Table 2, we report the results obtained on the application of equation 1 to the specific rates of solvolyses of **1** using the ten more nucleophilic solvents. We obtain an *l* value of 1.76 ± 0.28, an *m* value of 0.54 ± 0.15, a *c* value of 0.34 ± 0.15, an *F*-test value of 28, and an *R* value of 0.943. For **2** in the identical set of ten solvents we obtain, *l* = 1.89 ± 0.24, *m* = 0.55 ± 0.13, *c* = 0.27 ± 0.13, *F*-test = 46, and *R* = 0.964. The similarities of the *l* and *m* strongly indicates that **1** and **2** solvolyze by the same mechanism in these ten solvents and the magnitude of the *l* and *m* values are consistent with the addition step of an addition-elimination ($A_N + D_N$) mechanism being rate determining (Scheme 1). The slightly earlier tetrahedral transition state (Scheme 1) favored for **1** (when compared to that of **2**) is due to the polarizability of the sulfur atom and its ability to distort the shape of its electron cloud.

Table 2: Correlations of the specific rates of solvolysis of a variety of **1**, **2**, **3**, **4**, **5**, and **6** using the extended Grunwald-Winstein equation (equation 1).

Substrate	n^a	l^b	m^b	c^c	R^d	F^e	*Mechanism*
1	10	1.76 ± 0.28	0.54 ± 0.15	0.34 ± 0.15	0.943	28	A-E
	5	0.53 ± 0.18	0.89 ± 0.18	-2.66 ± 0.35	0.967	15	S_N1
2[f]	49	1.66 ± 0.05	0.56 ± 0.03	0.15 ± 0.07	0.980	568	A-E
3[g]	31	0.69 ± 0.05	0.95 ± 0.03	0.18 ± 0.05	0.987	521	S_N1
4[h]	16	1.74 ± 0.17	0.48 ± 0.07	0.19 ± 0.23	0.946	55	A-E
	6	0.62 ± 0.08	0.92 ± 0.11	-2.29 ± 0.13	0.983	44	S_N1
5[g]	9	1.88 ± 0.28	0.56 ± 0.15	0.38 ± 0.15	0.950	28	A-E
	18	0.34 ± 0.05	0.93 ± 0.09	-2.54 ± 0.34	0.955	77	S_N1
6[i]	22	1.32 ± 0.13	0.39 ± 0.08	-0.02 ± 0.10	0.952	95	A-E

[a] *n* is the number of solvents. [b] With associated standard error. [c] The earlier values are accompanied by standard error of the estimate. [d] Correlation coefficient. [e] *F*-test value. [f] Values taken from ref. 18. [g] Values taken from ref. 10. [h] Values taken from ref. 29. [i] Values taken from ref. 27.



Scheme 1: Stepwise addition-elimination mechanism through a tetrahedral intermediate for chlorothionoformate esters.

At 25.0 ^{o}C, the rates of solvolysis in 100% EtOH for **1**, **2**, **3**, **4**, **5**, and **6** are 11.9 ± 1.1 X 10^{-5} s^{-1}, 260 ± 3 X 10^{-5} s^{-1} [18], 0.996 ± 0.02 X 10^{-5} s^{-1} [10], 6.73 ± 0.15 X 10^{-5} s^{-1} [29], 3.15 ± 0.04 X 10^{-5} s^{-1} [10], and 1759 X 10^{-5} s^{-1} (estimated from the Arrhenius activation parameters reported in ref. 27) respectively. For substrates **1-6** it is proposed that the addition-elimination mechanism dominates in pure ethanol (Table 2). The corresponding ethanolysis rate order of $k_6 >> k_2 >> k_1 > k_4 > k_5 > k_3$ demonstrates the powerful inductive effects instigated by the presence of both a phenoxy group and a fluorine leaving group around the carbonyl carbon in **6** when compared to the electron-withdrawing effects witnessed in the tetrahedral addition-elimination transition-state of the other substrates. The observation that **1** is approximately four times faster than **5** in pure ethanol is consistent with a slightly positive Hammett σ_p value of + 0.06 [30] for *para*-F, implying a higher electron-withdrawing power of the *para*-substituted fluorine atom in **1** relative to the H in the *para* position in **5**.

A plot of log (k/k_o) for 4-fluorophenyl chlorothionoformate (**1**) against 1.76 N_T + 0.54 Y_{Cl} in the fifteen common pure and binary solvents studied is shown in Figure 3. The points for the 97, 90, 70 HFIP and 97, 90 TFE were not included in the correlation. They were added to show the extent of their deviation.

Application of equation 1 to the solvolysis of **1** in these five highly ionizing deviating fluoroalcohols results in l = 0.53 ± 0.18, m = 0.89 ± 0.18, c = -2.66 ± 0.35, F-test = 15, and R = 0.967 (Table 2). A large negative c value is observed because the experimental k_o value is the one applying to the other reaction channel. The large errors associated with the l and m values and the low F-test value are due to the very small number of solvents (five in this case) used for dual parameter analyses [19]. However, the ranges of these l and m values are very similar to those observed for the solvolyses of **3**, where an S_N1 ionization (D_N + A_N) mechanism with strong rear-side nucleophilic solvation was proposed.

We now assert that 1 undergoes solvolysis in 97%, 90%, and 70% HFIP, and 97% and 90% TFE, by an ionization (S_N1) mechanism with strong nucleophilic solvation of the resonance stabilized carbocation (Scheme 2). This proposal is in agreement with the slight increase in the specific rates of solvolysis that is observed as the water content increases (due to an increase in the nucleophilicity) in these mixtures.

On the other hand, it was shown [18] that **5** solvolyzes by the ionization pathway (Scheme 2) in a wider variety of ionizing solvents (when compared to the range of ionization observed in **1**) including the aqueous alcohols and water. This is due to the sulfur atom's lone-pair electron polarizability (in **5**) being more diffuse in the absence of the electron withdrawing fluorine atom in the *para* position, hence its ability to favor the resonance contributor 2b in Scheme 2.

4. Conclusion

4-Fluorophenyl chlorothionoformate (1) was shown to solvolyze by dual bimolecular addition-elimination (A_N + D_N) and unimolecular ionization (D_N + A_N) mechanisms whose dominance depended on the nucleophilicity and ionizing power of the solvent. The exact solvent compositions where the change in mechanism occurred were identified utilizing the similarity model concept and the extended Grunwald-Winstein equation.

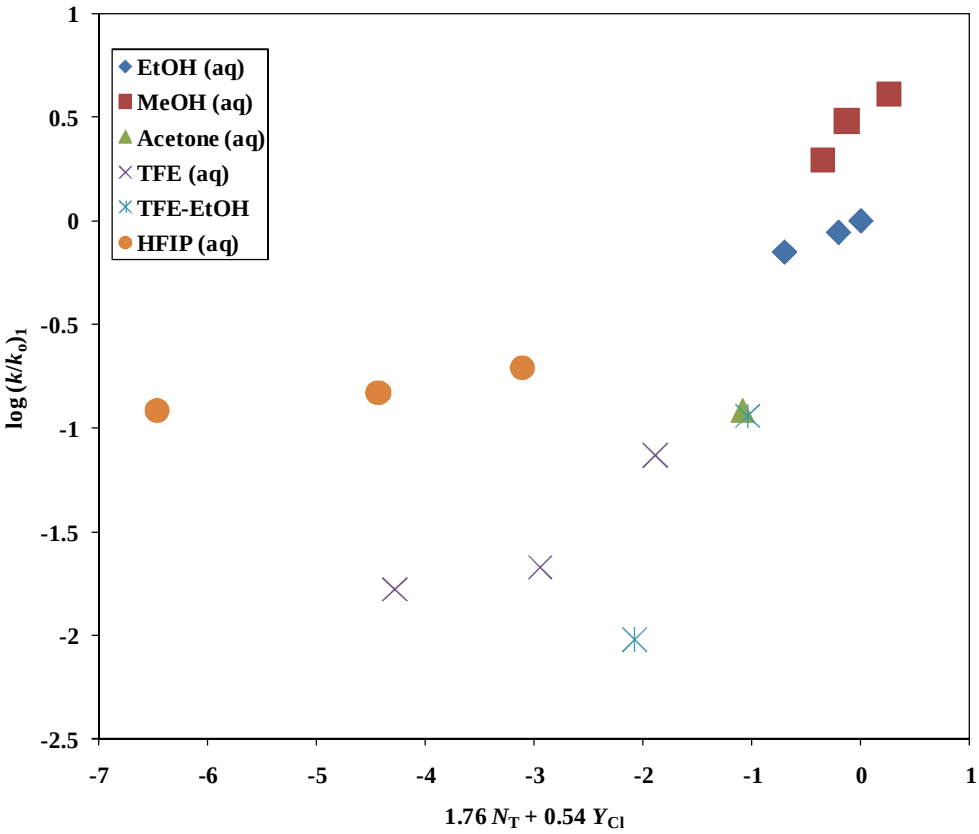
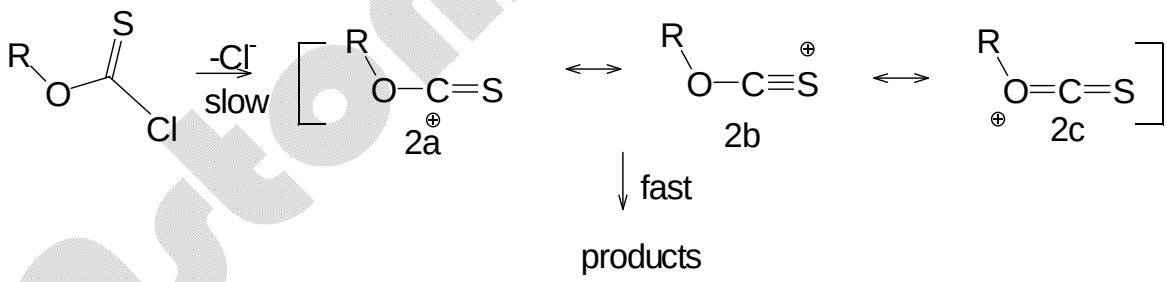


Figure 3: The plot of log (k/k_o) for 4-fluorophenyl chlorothionoformate (**1**) against 1.76 N_T + 0.54 Y_{Cl} in the fifteen common pure and binary solvents studied.



Scheme 2: Unimolecular step-wise solvolysis of chlorothionoformate esters.

Abbreviations

S_N1	substitution nucleophilic unimolecular
S_N2	substitution nucleophilic bimolecular
$A_N + D_N$	association-dissociation
$D_N + A_N$	dissociation-association
CNDO/2	"semi-empirical" all-valence electron-self-consistent-field theory
σ_p	Hammett sigma constant for *para* substituent
DE-INBRE	Delaware-IDeA Network of Biomedical Research Excellence

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

SMH and BPM completed this research under the direction of MJD as undergraduate research assistants in the DE-INBRE sponsored Wesley College Directed Research Program. DNK is a collaborator on this project.

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