Correlation of the Rates on Solvolysis of 2,2,2-Trichloroethyl Chloroformate Using the Extended Grunwald-Winstein Equation

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The solvolysis rate constants of 2,2,2-trichloroethyl chloroformate (Cl_3CCH_2OCOCl, **3**) in 30 different solvents are well correlated with the extended Grunwald-Winstein equation, using the N_T solvent nucleophilicity scale and the Y_{Cl} solvent ionizing scale, with sensitivity values of 1.28 ± 0.06 and 0.46 ± 0.03 for l and m, respectively. The activation enthalpies ($\Delta H^{\neq}$) are 10.1 to 12.8 kcal·mol^{-1} and the activation entropies ($\Delta S^{\neq}$) are -27.8 to -36.8 cal·mol^{-1}·K^{-1}, which is consistent with the proposed bimolecular reaction mechanism. The kinetic solvent isotope effect (k_{MeOH}/k_{MeOD}) of 2.39 is also in accord with S_N2 mechanism probably assisted by general-base catalysis.

Key Words : 2,2,2-Trichloroethyl chloroformate, Extended grunwald-winstein equation, S_N2 Mechanism, Solvent kinetic isotope effect

Introduction

Chloroformate esters (ROCOCl, **1**) are known to hydrolyze much slower than other acyl chlorides (RCOCl). Initial-state stabilization through π-electron resonance (**2**) has been suggested to be responsible for the reduced reactivity of **1**, because such a resonance interaction is not possible for RCOCl.[1] This resonance effect would be more significant as R in **1** becomes a stronger electron donating group but be insignificant when R is a strong electron withdrawing group. The electronic nature of R would also cause a change in the reaction mechanism, *i.e.*, from rate-limiting breakdown of a tetrahedral intermediate to rate-limiting formation of an intermediate upon introducing a strong electron donating group, R.[2]

The overall picture of products formed from **1** is shown in Scheme 1, with pathways involving substitution at the acyl carbon shown on the left hand side (bimolecular) and pathways involving the direct loss of carbon dioxide accompanying the substitution on the right hand side (unimolecular).[3]

The possible products formed for the solvolyses of several chloroformate esters is shown in Eq. (1).
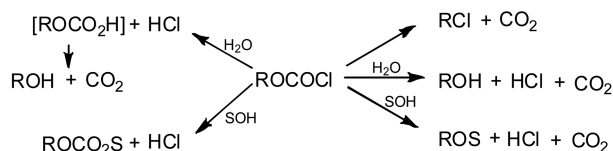
$$ROCOCl + SOH/H_2O \rightarrow$$
$$ROCOOS + ROS + ROH + CO_2 + HCl \qquad (1)$$

The dialkyl or alkyl aryl carbonate is formed by nucleophilic attack of alcohol (SOH) at the acyl carbon. The alcohol or phenol product is formed either by a parallel attack of water to give the hydrogen carbonate ester, followed by the loss of CO_2,[4] or by the attack of water on R^+, formed by the loss of CO_2 from an intermediate carboxylium ion $(ROCO)^+$. The capture of the R^+ by SOH leads to the ester (ROS) whereas the capture of the R^+ by the chloride ion formed in the ionization leads to RCl through a decomposition pathway (for the chloroformate ester reactant). An alternative decomposition pathway, involving the extraction of a β-proton from the R group and alkene formation, could also occur.

Two types of mechanism have been found to operate, postulated as an addition-elimination mechanism (Scheme 2) with the addition being rate determining and an ionization mechanism[5] (Scheme 3).

In view of the often suggested mechanistic change for solvolysis of chloroformate esters from rate-limiting ionization (for alkyl groups R in ROCOCl with concurrent or subsequent fragmentation) to addition-elimination with the
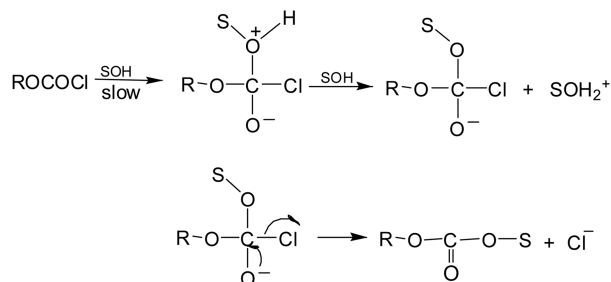
If S=H, this is followed by R-O-C(=O)-O-H → ROH + CO₂

Scheme 2
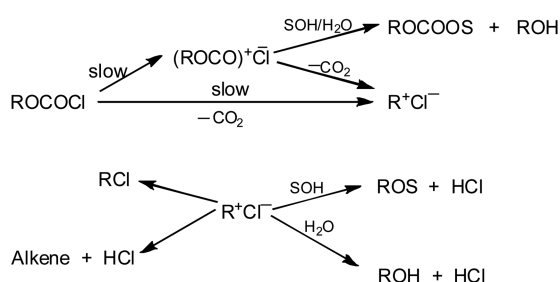
Scheme 1

Scheme 3

addition step rate-limiting, it would be interesting to conduct kinetic studies on the solvolysis reactions of 2,2,2-trichloro-ethyl chloroformate (**3**) in pure and mixture solvents. For non-solvolytic substitutions, it has been proposed that a variation in the R of ROCOX can lead to a change in the late-limiting step from addition to elimination within the addition-elimination mechanism.[2]

2,2,2-Trichloroethyl chloroformate (**3**) can be considered as a derivative of ethyl chloroformate, with the methyl group replaced by a trichloromethyl group. This involves replacing a group (CH_3-) with a Taft polar substituent constant of zero (by definition) with a group (Cl_3C-) with a very large positive value of 2.65.[6] This will cause an enormous difference in the electronic effects of the alkyl group according to the substituents.

The ethyl chloroformate decomposes rapidly at room temperature with the ejection of carbon dioxide to form isobutylene and hydrogen chloride.[7] Replacement of the ethyl group by the bridgehead 1-adamantyl group gives a more stable tertiary chloroformate ester. The kinetic and the product studies of its decomposition in inert solvents[8] and of its solvolyses[9] indicate an ionization-fragmentation mechanism in a wide range of solvents. Only in 100% ethanol, a small amount of the dicarbonate formed by the attack of the solvent at the acyl carbon was observed. It would be interesting to investigate the effects of the three chlorine atoms introduced into the ethyl group of **3** as well as leading, due to the powerful electron-withdrawing properties of the trichloromethyl group, to a considerably reduced tendency to ionization and to a partial or complete switch to the addition-elimination pathway.

To gain further understanding of the mechanism of acyl transfer, we have carried out a kinetic study on the solvolysis of 2,2,2-trichloroethyl chloroformate in a variety of pure and binary solvents at 35.0 °C [eqn. (2)]. We have determined the *l* and *m* values in the extended Grunwald-Winstein equation[1] [eqn. (3)], together with the enthalpies and the entropies of activation, and the solvent kinetic isotope effect (SKIE).
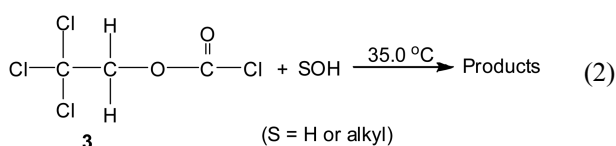
$$\log (k/k_o) = l\,N_T + m\,Y_{Cl} \qquad (3)$$

In Eq. (3), *k* and k_o represent the rate constants of solvolysis in a given solvent and in a standard solvent (80% ethanol), respectively; *l* represents the sensitivity to changes in solvent nucleophilicity (N_T); *m* represents the sensitivity to changes in the solvent ionizing power (Y_X, for a leaving group X).

Results and Discussion

The rate constant (*k*) for solvolysis of **3** in 34 pure and binary solvents at 35.0 °C are summarized in Table 1. The constant, *k* increases as the ratio of water in the solvents

Table 1. Rate constants of solvolysis of 2,2,2-trichloroethyl chloroformate[a] in a variety of pure and mixed solvents at 35.0 °C and the N_T and the Y_{Cl} values for the solvents

Solvent[b]	$10^2\,k^c$ (s⁻¹)	N_T[d]	Y_{Cl}[d]
100%EtOH	0.417±0.004	0.37	-2.52
90%EtOH	0.977±0.005	0.16	-0.94
80%EtOH	1.23±0.02	0.0	0.0
70%EtOH	1.35±0.03	-0.20	0.78
60%EtOH	1.58±0.02	-0.38	1.38
50%EtOH	1.86±0.04	-0.58	2.02
40%EtOH	2.24±0.03	-0.74	2.75
20%EtOH	3.80±0.03	-1.16	4.09
100%MeOH[e]	1.15±0.02	0.17	-1.20
90%MeOH	2.57±0.05	-0.01	-0.20
80%MeOH	3.89±0.03	-0.06	0.67
70%MeOH	4.17±0.04	-0.40	1.46
50%MeOH	6.17±0.04	-0.75	2.70
40%MeOH	7.24±0.07	-0.87	3.25
20%MeOH	9.33±0.05	-1.23	4.10
90%Acetone	0.0741±0.0003	-0.35	-2.39
80%Acetone	0.186±0.003	-0.37	-0.83
70%Acetone	0.407±0.004	-0.42	0.17
60%Acetone	0.676±0.005	-0.52	1.00
50%Acetone	1.17±0.04	-0.70	1.73
40%Acetone	1.86±0.04	-0.83	2.46
30%Acetone	3.24±0.03	-0.96	3.21
20%Acetone	4.68±0.05	-1.11	3.77
90%TFE[f]	0.0347±0.0004	-2.55	2.85
80%TFE	0.0490±0.0005	-2.19	2.90
70%TFE	0.0631±0.0004	-1.98	2.96
50%TFE	0.129±0.003	-1.73	3.16
90%HFIP[f]	0.00389±0.00003	-3.84	4.31
70%HFIP	0.0117±0.0002	-2.94	3.83
50%HFIP	0.0372±0.0003	-2.49	3.80
80T-20E[g]	0.0148±0.0003	-1.76	1.89
60T-40E	0.0437±0.0004	-0.94	0.63
40T-60E	0.105±0.002	-0.34	-0.48
20T-80E	0.245±0.002	0.08	-1.42

Unless otherwise indicated, a 1.0 mol dm⁻³ solution of the substrate in the indicated solvent, containing 0.1% CH_3CN. On a volume-volume content at 25.0 °C, and the other component is water. With associated standard deviations. Values from ref. 10. Values of $k = 4.82(\pm 0.03) \times 10^{-3}$ s⁻¹ in deuterated methanol (MeOD), corresponding to k_{MeOH}/k_{MeOD} value of 2.39 ± 0.03 (with associated standard error).[20] Solvent prepared on a weight-weight basis at 25.0 °C, and the other component is water. T-E represents TFE-ethanol mixtures.

increases. This indicates that solvent-ionizing power is more important than solvent nucleophilicity because water has much stronger ionizing power than other solvents employed in this study.[10]

In the present study, we measured the rate constants of the solvolysis represented in Eq. (2) using automatic conductivity apparatus. In most solvents, the reactions proceeded rapidly, which enabled us to record the responses as a function of time.[11] In order to promote a rapid dissolution in the solvent, the substrate was added as a small volume of a concentrated stock solution in acetonitrile so that the reaction solution contained about 0.1% acetonitrile.

The rate constant for ethanolysis of **3** measured in this study was 2.31×10^{-3} s^{-1} at 25.0 °C (Table 2), which is much larger than that previously reported for benzyl chloroformate ($C_6H_5CH_2OCOCl$)[12] ($k = 5.16 \times 10^{-5}$ s^{-1} at 25.0 °C). This suggests that the 2,2,2-trichloroethyl group has more electron-withdrawing power than the benzyl group and therefore it would be more favorable for nucleophilic attack at the electron-deficient carbonyl carbon.

The activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, calculated from the k values at four different temperatures for solvolysis of **3** in pure EtOH and MeOH, and in 80%EtOH and 70%TFE are shown in Table 2. The values of $\Delta H^{\neq}$ was relatively low (10.1 to 12.8 kcal·mol^{-1}) and the values of $\Delta S^{\neq}$ was largely negative (−27.8 to −36.8 cal·mol^{-1}K^{-1}), being within the ranges of previously reported results for a normal S$_N$2 reaction.[13] In deuterated methanol (MeOD), a solvent kinetic isotope effect (k_{MeOH}/k_{MeOD}) of 2.39 ± 0.04 was observed at 35.0 °C. This is within the SKIE values of 1.58-2.31,

Figure 1. Plot of log (k/k_o) *versus* 1.28 N$_T$ + 0.46 Y$_{Cl}$ for the solvolysis of 2,2,2-trichloroethyl chloroformate.

reported for the corresponding methanolyses of *n*-propyl chloroformate and a series of benzenesulfonyl chlorides at 25.0 °C in which the reactions are believed to be S$_N$2 in character.[14]

The extended Grunwald-Winstein equation [eqn. (3)] is useful to determine the extent of a nucleophilic participation by the solvent because the magnitudes of *l* and *m* in Eq. (3) are the indicators to determine whether a nucleophilic substitution reaction proceeds through a unimolecular, S$_N$1 (*i.e.*, $l \approx 0$ and $m \approx 1$) or a bimolecular reaction, S$_N$2 (*i.e.*, $l \approx 1.3$ and $m \approx 0.5$). Therefore, the determination of *l* and *m* values would provide valuable information concerning the structure of the transition state for solvolyses.[14]

Application of Eq. (3)[10] to the solvolysis of **3** led to only moderately good correlations, with dispersal of data for different binary mixtures. For 34 solvents, *l* and *m* values were 1.34 ± 0.07 and 0.50 ± 0.04, respectively and the correlation coefficient (R) was 0.957. Close inspection showed that the four data points for solvolysis in TFE-ethanol mixtures lay below the plot. When these points were omitted in the correlation, better correlation coefficient (R = 0.973) was obtained with *l* and *m* values of 1.28 ± 0.06 and 0.46 ± 0.03, respectively. In earlier correlations of other solvolyses, data points for these TFE-ethanol solvent systems usually lay below the correlation line.[15] Sensitivity values, *l* and *m* are tabulated in Table 3, and compared with other values reported for similar substrates.

The *l* value of 1.28 and the *m* value of 0.46 of **3** were smaller than those recently reported for reactions proceeding through an addition-elimination mechanism ($l = 1.56$-1.68

Table 2. Rate constants and activation parameters for the solvolysis of 2,2,2-trichloroethyl chloroformate[a] at various temperatures

Solvent (%)	Temp. (°C)	$10^2 k^{(b)}$ (s^{-1})	$\Delta H^{\neq}$ (kcal·mol^{-1})[c]	$-\Delta S^{\neq}$ (cal·mol^{-1}·K^{-1})[c]
100EtOH	25.0	0.231±0.002	11.0±0.4	33.9±1.5
	35.0	0.417±0.004		
	45.0	0.767±0.003		
	55.0	1.42±0.03		
80EtOH[d]	25.0	0.711±0.005	10.1±0.4	36.8±1.3
	35.0	1.23±0.02		
	45.0	2.17±0.03		
	55.0	3.80±0.02		
100MeOH	25.0	0.605±0.003	11.8±0.5	30.9±1.6
	35.0	1.15±0.02		
	45.0	2.21±0.02		
	55.0	4.29±0.03		
70TFE[e]	25.0	0.00329±0.00002	12.8±0.5	27.8±1.7
	35.0	0.00631±0.00004		
	45.0	0.0133±0.0002		
	55.0	0.0265±0.0003		

(a) A 1.0 mol dm^{-3} solution of the substrate in the indicated solvent, also containing 0.1% CH$_3$CN. (b) Averages of three or more runs, with standard deviation. (c) The activation parameters are accompanied by the standard error. (d) On a volume-volume content at 25.0 °C, and the other component is water. (e) Solvent prepared on a weight-weight basis at 25.0 °C, and the other component is water.
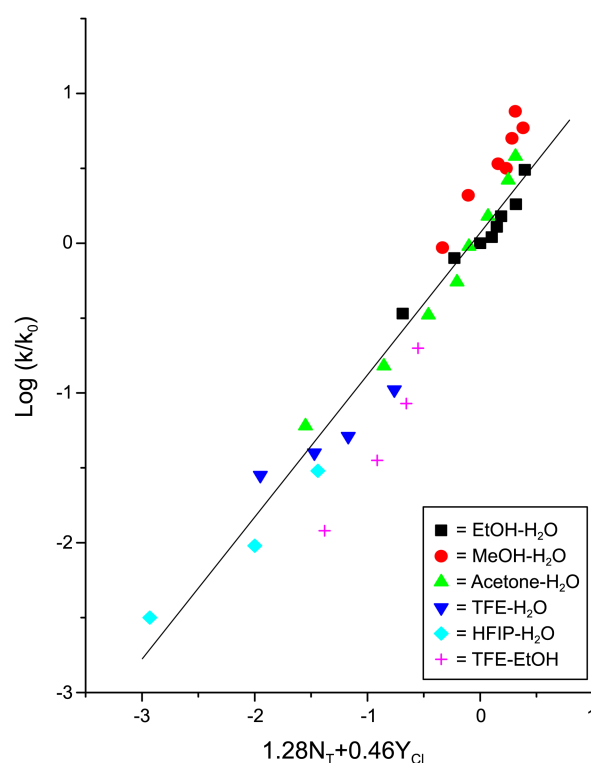
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Table 3. Extended Grunwald-Winstein correlations of the kinetics of solvolytic displacement of chloride

Substrate	n^a	l^b	m^b	l/m	R^c
2-AdOCOCl[d]	19	~0	0.47±0.03	~0	0.970
i-PrOCOCl[e]	20	0.28±0.05	0.52±0.03	0.54	0.979
9-Fluorenyl-OCOCl[f]	30	0.95±0.07	0.38±0.04	2.5	0.941
((CH₃)₂N)₂POCl[g]	27	1.14±0.05	0.63±0.03	1.8	0.982
CH₃SO₂Cl[h]	43	1.20±0.05	0.52±0.03	2.3	0.969
(CH₃)₂NSO₂Cl[i]	32	1.20±0.04	0.72±0.03	1.7	0.985
C₆H₅PCl[j]	25	1.25±0.09	0.46±0.06	2.7	0.954
(C₆H₅O)₂POCl[k]	29	1.31±0.10	0.61±0.04	2.1	0.960
(CH₃O)₂PSCl[l]	28	1.16±0.08	0.55±0.03	2.1	0.966
Cl₃CCH₂OCOCl[m]	34	1.34±0.07	0.50±0.04	2.7	0.957
Cl₃CCH₂OCOCl[m]	30	1.28±0.06	0.46±0.03	2.8	0.973
CH₃OCOCl[i]	19	1.59±0.09	0.58±0.05	2.7	0.977
C₆H₅OCOCl[n]	21	1.68±0.10	0.57±0.06	3.0	0.973
C₂H₅OCOCl[o]	28	1.56±0.09	0.55±0.03	2.8	0.967
n-OctOCOCl[p]	19	1.67±0.07	0.76±0.03	2.2	0.988

[a]Number of solvents. [b]From equation (3) and with associated standard error. [c]Multiple correlation coefficient. [d]Ref. 3. [e]Ref. 16e. [f]Ref. 21. [g]Ref. 15. [h]Ref. 18. [i]Ref. 13a. [j]Ref. 2. [k]Ref. 23. [l]Ref. 19. [m]This work. [n]Ref. 13. [o]Ref. 16. [p]Ref. 24.

and $m = 0.55$-0.76), whereas these values were similar to those previously reported for the bimolecular solvolyses of other substrates (Table 3). This suggests an S_N2 mechanism involving nucleophilic attack by the solvent at carbonyl carbon atom of **3**. The solvolysis of **3**, where bond making ($l = 1.28$) is more progressed than bond breaking ($m = 0.46$), and the values are still in the range of S_N2 mechanism, reflecting on the degree of the nucleophilic assistance based on the measure of solvent nucleophile.[16]

The lower m value ($m = 0.46$) for the solvolysis of **3**, compared to n-octyl fluoroformate ($m = 0.76$),[5] phenyl chloroformate ($m = 0.53$),[13a] methyl chloroformate ($m = 0.58$),[17] and ethyl chloroformate ($m = 0.55$),[16] may reflect a reduced need for solvation of the developing negative charge on the carbonyl oxygen (see Table 3).

The l/m ratio has been suggested as a useful mechanistic criterion.[13-16] For the solvolysis of **3**, the l/m value was calculated to be 2.8, which is similar to those of *N,N*-dimethyl sulfamoyl chloride ((CH₃)₂NSO₂Cl),[16] methylsulfonyl chloride (CH₃SO₂Cl),[18] dimethyl thiophosphorochloridate ((CH₃O)₂PSCl),[19] and *N,N,N',N*-tetramethyldiamidophosphorochloridate ((CH₃)₂N)₂POCl),[15] to suggest the S_N2 mechanism.

In addition, the $k_{80\%EtOH}/k_{100\%EtOH}$ ratio has also been suggested as a useful mechanistic criterion.[13-16] The $k_{80\%EtOH}/k_{100\%EtOH}$ values of 95 to 320 can be considered to represent the S_N1 reaction or the ionization pathway.[10a,d] In contrast, several $k_{80\%EtOH}/k_{100\%EtOH}$ values were reported for the proposed S_N2 reactions: solvolyses of methyl chloroformate (4.0),[16] ethyl chloroformate (3.2),[16] benzyl chloroformate (3.4),[12] π-methylbenzoyl chloride (5.3).[14] These values ($k_{80\%EtOH}/k_{100\%EtOH} = 3.2$-$5.3$) have less sensitivity due to the solvent ionizing power. The $k_{80\%EtOH}/k_{100\%EtOH}$ value of 3.0 obtained for the solvolysis of **3** is similar to those obtained

from the four substrates that are believed to proceed through S_N2 mechanism.

Conclusions

Application of the extended Grunwald-Winstein equation (3) to the solvolysis of **3** led to an l value of 1.28 and an m value of 0.46. These values were smaller than those reported for reactions proceeding through an addition-elimination mechanism ($l = 1.56$-1.68 and $m = 0.55$-0.76, Table 3). Therefore, one can conclude that solvolysis of **3** proceeds through an S_N2 mechanism (TS 1), in which bond making is more progressed than bond breaking on the bases of the magnitudes of l and m.[10] This conclusion can be further supported by a resonable activation parameters (*i.e.*, relatively small $\Delta H^{\neq}$ and large negative $\Delta S^{\neq}$) and the solvent kinetic isotope effect (2.39).
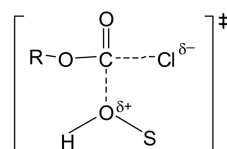
TS 1

Experimental

Solvents were purified as previously described.[14] The 2,2,2-trichloroethyl chloroformate (**3**, Aldrich 98%) was used as received. The kinetic experiments were carried out by allowing a conductivity cell containing 12.5 mL of solvent to equilibrate, with stirring, in a constant-temperature water bath. A 12 μL portion of a 1.0 mol dm⁻³ stock solution of **3** in acetonitrile was then added. The monitoring of increases in conductivity with time and the calculation of the rate constants were conducted as previously reported.[14] The multiple regression analyses were performed using commercially available packages.

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