

Stoichiometric Effects. Correlation of the Rates of Solvolysis of Isopropenyl Chloroformate

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Solvolysis rates of isopropenyl chloroformate (**3**) in water, D₂O, CH₃OD and in aqueous methanol, ethanol, 2,2,2-trifluoroethanol (TFE), acetone, 1,4-dioxane as well as TFE-ethanol at 10 °C are reported. Additional kinetic data for pure water, pure ethanol and 80%(w/w) 2,2,2-trifluoroethanol (T)-water (W) at various temperatures are also reported. These rates show the phenomena of maximum rates in specific solvents (30% (v/v) methanol-water and 20% (v/v) ethanol-water) and, variations in relative rates are small in aqueous alcohols. The kinetic data are analyzed in terms of GW correlations, steric effects, kinetic solvent isotope effects (KSIE), and a third order model based on general base catalysis (GBC). Solvolyses based on predominately stoichiometric solvation effect relative to medium solvation are proceeding in **3** and the results are remarkably similar to those for *p*-nitrobenzoyl chloride (**4**) in mechanism and reactivity.

Key Words : Solvolyses, Grunwald-Winstein correlation parameters, Stoichiometric effect, Isopropenyl chloroformate

Introduction

The two-term (extended) Grunwald-Winstein (GW) equation (1)^{1,2} as a free energy relationship is a very useful tool in studies of solvolytic displacement reactions, where one or more components of the solvent functions have not only as the reaction medium, but also as a nucleophilic reagent leading to substitution.

$$\log(k/k_0) = mY_{Cl} + lN_T + c \quad (1)$$

In equation (1) *k* and *k*₀ are rate constants of solvolyses of a substrate RX in a given solvent and 80% (v/v) ethanol-water, respectively; *m* is the susceptibility to change in ionizing power (*Y*_{Cl}: based on solvolysis of 1-adamantyl chloride³ with *m* = 1.00); *l* is the susceptibility to change in solvent nucleophilicity (*N*_T) (*N*_T: based on the solvolyses of S-methyl dibenzothiophenium ion²); and *c* is a constant (residual term).

The successful application of two-term GW correlation to nucleophilic assistance by solvent at acyl (sp²-hybridized) carbon, where evidence has been obtained for both ionization and addition-elimination (*l* value about 1.5 to 1.7) pathways being rate-determining, have been reported.⁴

Recently, studies of solvent effect and mechanism through correlations of the rates of solvolysis of substituted acetyl chlorides^{5,6,7} (with sp²-hybridized carbon as reaction center) analyzed by the two-term treatment (eq. 1) showed that the reactivity appears to be affected by steric effects and/or that, according to the kind of substituents (aliphatic- or phenyl-group) and solvent systems studied, there are marked differences in solvation effect and mechanism. Whereas, in case of solvolytic reactions of substituted acetyl chlorides including S-atom, the reaction with the same mechanism (S_N2 reaction) controlled by a similarity of solvation of TS

was reported,⁷ regardless of the kind of neighboring group (alkyl group or aromatic ring).

Also, more recently, our result⁸ for correlation of solvolysis rates of 2-chloro thioacetophenone with sp³-hybridized carbon as reaction center [the introduction of carbonyl (C=O) group as well as including S-atom] using the two-term (extended) GW plot (eq. 1) estimated that mechanistic change may be influenced by the kind of neighboring group (CH₃- or Ph-group). Other results studied by Kevill and Kim⁹ have shown that the introduction of benzoyl group (PhC=O) into methyl bromide (tosylate) leading phenacyl bromide (tosylate) do not appear to be affected by inductive effect (electronic effect) on the reactivity, but do vary in steric effect, and supporting evidence arises from the two-term correlation (eq. 1) for solvolytic reactions.

These results increase current interest in kinetic studies of sterically-hindered compounds, which reacts by bimolecular reaction with nucleophilic assistance.

Accordingly, we attempt to investigate further for solvolyses of isopropenyl chloroformate (**3**) (C=O; sp²-hybridized carbon), which is the introduction of a double bond in carbon-carbon into isopropyl chloroformate (**2**) proposed as a dual reaction channel. We investigated 46-solvent systems at 10 °C and additional kinetic data in pure water, pure ethanol and 80%(w/w) trifluoroethanol (T)-water (W) at various temperatures are also reported. These kinetic data are analyzed in terms of GW correlation, steric effect, kinetic solvent isotope effect (KSIE), and a third order model based on GBC.

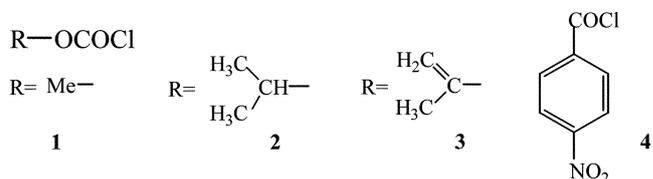


Table 1. The rate constants (k/s^{-1}) for solvolysis of isopropenyl chloroformate (**3**) in binary solvent mixtures at 10.0 °C^a

solvent composition (% (v/v))	rate constant (k/s^{-1})		
	methanol-water	ethanol-water	acetone-water
100	$(7.40 \pm 0.06) \times 10^{-4}$	$(2.07 \pm 0.10) \times 10^{-4}$	–
90	$(1.27 \pm 0.03) \times 10^{-3}$	$(3.92 \pm 0.05) \times 10^{-4}$	$(9.33 \pm 0.03) \times 10^{-6}$
80	$(1.58 \pm 0.03) \times 10^{-3}$	$(4.68 \pm 0.03) \times 10^{-4}$	$(6.50 \pm 0.02) \times 10^{-5}$
70	$(1.90 \pm 0.06) \times 10^{-3}$	$(5.20 \pm 0.07) \times 10^{-4}$	$(1.10 \pm 0.04) \times 10^{-4}$
60	$(2.11 \pm 0.04) \times 10^{-3}$	$(6.60 \pm 0.03) \times 10^{-4}$	$(1.83 \pm 0.05) \times 10^{-4}$
50	$(2.29 \pm 0.01) \times 10^{-3}$	$(7.75 \pm 0.03) \times 10^{-4}$	$(2.90 \pm 0.06) \times 10^{-4}$
40	$(2.54 \pm 0.05) \times 10^{-3}$	$(1.08 \pm 0.20) \times 10^{-3}$	$(4.60 \pm 0.05) \times 10^{-4}$
30	$(2.59 \pm 0.03) \times 10^{-3}$	$(1.42 \pm 0.01) \times 10^{-3}$	$(7.00 \pm 0.02) \times 10^{-4}$
20	$(2.10 \pm 0.06) \times 10^{-3}$	$(1.58 \pm 0.01) \times 10^{-3}$	$(8.33 \pm 0.06) \times 10^{-4}$
10	$(1.24 \pm 0.02) \times 10^{-3b}$	$(1.53 \pm 0.04) \times 10^{-3b}$	$(1.09 \pm 0.06) \times 10^{-3b}$
0	$(1.16 \pm 0.02) \times 10^{-3c}$	$(1.16 \pm 0.02) \times 10^{-3c}$	$(1.16 \pm 0.02) \times 10^{-3c}$
	MeOD	D ₂ O ^e	
100	$(3.17 \pm 0.08) \times 10^{-4}$	$(5.57 \pm 0.13) \times 10^{-4}$	
	TFE – water ^d	TFE – ethanol ^e	1,4-dioxane-water
80	5.14×10^{-6f}	$(2.45 \pm 0.20) \times 10^{-6}$	–
70	$(1.38 \pm 0.17) \times 10^{-5}$	$(8.07 \pm 0.30) \times 10^{-6}$	–
60	$(2.50 \pm 0.05) \times 10^{-5}$	$(1.98 \pm 0.15) \times 10^{-5}$	–
50	$(5.31 \pm 0.01) \times 10^{-5}$	$(4.00 \pm 0.10) \times 10^{-5}$	–
40	$(1.01 \pm 0.15) \times 10^{-4}$	$(6.31 \pm 0.15) \times 10^{-5}$	–
30	–	$(4.00 \pm 0.01) \times 10^{-5}$	$(6.90 \pm 0.07) \times 10^{-4}$
20	–	$(1.30 \pm 0.01) \times 10^{-4}$	$(7.60 \pm 0.09) \times 10^{-4}$
10	–	–	$(1.01 \pm 0.02) \times 10^{-3b}$

^aDetermined conductimetrically at least in duplicate typically injected 4 μ L of 10% (w/w) substrate in dry acetonitrile into the kinetic apparatus, with a turbo-stirrer containing 2 mL of each solvent mixture; errors shown are average deviation. ^bInjected 4 μ L of 5% (w/w) substrate in dry acetonitrile. ^cInjected 4 μ L of 3% (w/w) substrate in dry acetonitrile. ^dSolvent composition w/w% by trifluoroethanol (water contents were confirmed as errors $\leq 0.3\%$ by using Karl Fisher Titrator). ^eSolvent composition v/v% by alcohol (trifluoroethanol). ^fExtrapolated from data given in Table 4.

Results and Discussion

The results analyzed for solvolysis rate constants for **3**, over a full range of solvent systems used in this work, using

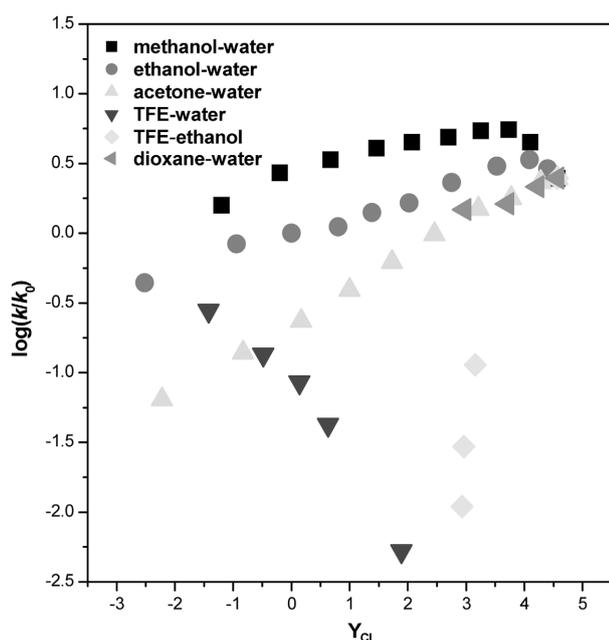


Figure 1. Plots of $\log(k/k_0)$ for solvolyses of isopropenyl chloroformate (**3**) at 10 °C against Y_{Cl} .

a original GW plot,¹ show dispersion phenomena (see Figure 1).

Solvolyses of **3** in methanol- and ethanol-waters show the phenomena of maximum rates in specific solvent compositions (30M and 20E)¹⁰ and low relative rates (≤ 8 -fold), as water is added gradually to alcohol solvent (see Table 1). Also, dispersion into separate line observed, with remarkably small values (for bimolecular reactions) of $m = 0.09 \pm 0.01$ (correlation coefficient, $r = 0.993$) for 90M-40M solvent systems and $m = 0.13 \pm 0.01$ ($r = 0.993$) for aqueous ethanol systems; nevertheless, the compound (**3**) has the possibility for steric effect (ionization) on reactivity.

The two term GW plots for solvolyses of **3** in a wide range of aqueous solvent system including 2,2,2-trifluoroethanol (TFE)-ethanol (EtOH) solvent mixtures are evaluated as an acceptable linear correlation ($r = 0.969$, $n = 40$) with $\log(k/k_0) = (0.60 \pm 0.03)Y_{Cl} + (1.88 \pm 0.09)N_T + 0.25 \pm 0.05$.

These results bring out nucleophilic solvation as main cause of dispersion in the mY_{Cl} plot for solvolyses of **3**. And our result for correlation of the rate of solvolysis of **3** at 10 °C is similar to those reported previously for *p*-nitrobenzoyl chloride (**4**)^{12b} at 25 °C with $\log(k/k_0) = 0.54Y_{Cl} + 1.78N_T + 0.11$. Also, the fractional contribution from solvent nucleophilicity gives identical values of 0.76 (Table 2). This probably means the prediction for similar mechanism, and the m and l values given by the two-term (eq. 1) correlation analysis in solvolysis rates of **3** provides a significant

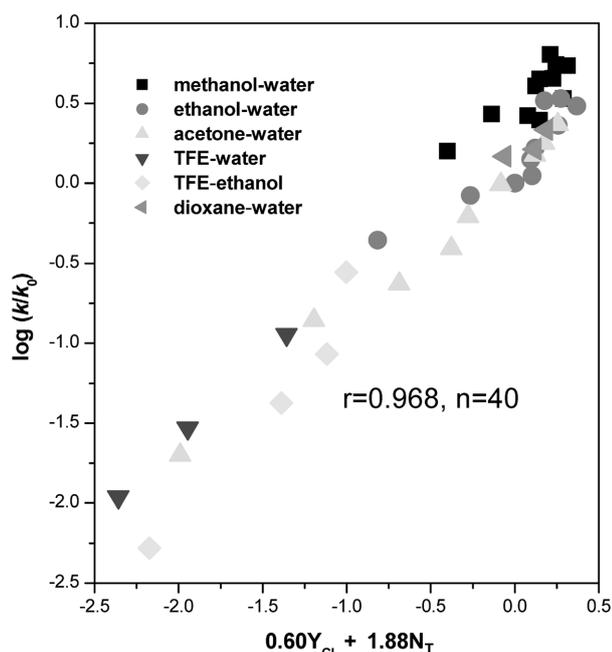


Figure 2. Plot of $\log(k/k_0)$ for solvolyses of isopropenyl chloroformate (**3**) at 10 °C against $(0.60Y_{Cl} + 1.88N_T)$.

information for the degree of low charge separation in the transition state (TS) structure in bimolecular reaction. The m - and l -values for solvolyses of chloroformate compounds with S_N pathway have been reported as 0.57, 1.68 for PhOCOCl ,¹¹ 0.58, 1.59 for MeOCOCl ¹³ and 0.46, 1.61 for $p\text{-NO}_2\text{PhOCOCl}$,¹⁴ respectively

Also, over a wide variety of solvent, correlation for the rate of solvolysis of methyl toylate (MeOTs), which was known well as S_N2 model compound, using the two-term (extended) treatment (eq.1) was reported as high m value of 0.54,¹² rather than the m value of 0.3 selected for the definition of N_{OTs} as solvent nucleophilicity parameter ($N_{OTs} = \log(k/k_0) - 0.3Y_{OTs}$).¹⁴ Accordingly, if N_T is employed, a

Table 2. Correlation analyses for solvolyses^a for isopropenyl chloroformate (**3**) at 10 °C using the two-term Grunwald-Winstein equation (1)

$\log(k/k_0) = mY_{Cl} + lN_T + c$					
m (A)	l (B)	c	n^b	r^c	$B/(A+B)^d$
0.60 ± 0.03	1.88 ± 0.09	0.25 ± 0.05	40 ^e	0.968	0.76

^aPerformed using Origin 6.0 program for multiple regression analysis and values of solvent parameter Y_{Cl} and N_T are quoted from ref 2, 3 and 11. ^bNumber of solvent. ^ccorrelation coefficient. ^dFraction of the contribution from solvent nucleophilicity. ^eUsing kinetic data over a full range of solvent chosen for this reaction.

high m - value of approximately 0.6 for **3** may be regarded as essential value for solvolytic reaction proceeding through S_N -type mechanism.

To investigate the effect of steric-hindrance effect¹⁵ of aliphatic groups adjacent to the site of nucleophilic attack from the rear, relative rates for solvolytic reaction of aliphatic substituted acyl chloride and chloroformate compounds in pure ethanol (highly nucleophilic assistance) are tabulated in Table 3. Substituent effects for acyl chlorides are a combination of electronic and steric effects, with the strong possibility of mechanistic changes.

About 15-fold value for **3** contrast with the other compound investigated in rate-ratio (k_{iso}/k_n) trend with a less than unity value (< 1) and ratio of susceptibility (l/m) trends for GW correlation (except for sulfonyl system in Table 3) also contrast with those.

According to the introduction of carbon-carbon double bond ($\text{C}=\text{C}$) group into isopropyl chloroformate (**2**), this solvolytic reaction for **3** does not appear to be affected by the steric factor, inhibiting the bimolecular reaction, but may be primarily influenced by the inductive effect, and then accelerated by nucleophilic participation on the reaction center led to a tighter transition state (TS).

More possible evidence for these interpretation arise from a value about 38 times (about 20 times) in ethanolysis

Table 3. Rate-ratio (k_{iso}/k_n) between solvolytic reaction for secondary (iso) and primary (n) aliphatic acid chloride and chloroformate compounds in a pure ethanol, kinetic solvent isotope effect (KSIE) and ratio of susceptibility (l/m) for correlation using the two-term Grunwald -Winstein equation (1)

Compound		T/°C	k_{iso}/k_n	l/m (n) ^a	KSIE	
					$k_{\text{MeOH}}/k_{\text{MeOD}}$	$k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$
RSO ₂ Cl	Me- ^b	25	4.54×10^{-3}	1.48 ^c (29)	1.62	1.80
	<i>i</i> -Pr- ^d			3.2 (29)	2.54	1.66
RCOCl	Me- ^e	0	0.77	1.18 (20)	1.32 ^f	—
	<i>i</i> -Pr- ^e			0.90 ^g (6)	1.37 ^g	—
	Bu- ^e			0.082 ^h	1.46 ^f	—
ROCOCl	Me-(1) ⁱ	40	0.104	2.74 (19)	—	1.89 ^{j,k}
	<i>i</i> -Pr-(2) ^l			0.54 (20)	—	1.35 ^j
	$\text{CH}_2=\text{C}(\text{CH}_3)$ -(3)			15.4 ^m	3.13 (40)	2.33 ^o

^aNumber of solvent used for correlation. ^bQuoted from ref. 16a. ^cAnalyzed from a data of and result obtained show $\log(k/k_0) = (0.23 \pm 0.03) Y_{Cl} + (0.34 \pm 0.11) N_T + (0.034 \pm 0.03)$ using Grunwald-Winstein correlation. ^dQuoted from ref. 16b. ^eQuoted from ref. 5. ^fQuoted from ref. 7. ^gQuoted from ref. 6 and analyzed in fluorinated solvent mixtures as $\log(k/k_0) = (0.81 \pm 0.10) Y_{Cl} + (0.72 \pm 0.08) N_T + c$. ^hRate-ratio of $k_{\text{Me}}/k_{\text{t-Bu}}$. ⁱQuoted from ref. 13. ^jQuoted from ref. 17: at 24.5 °C. ^kQuoted from ref. 17: $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.79$ at 7.5 °C for PhOCOCl . ^lQuoted from ref. 18. ^mRate-ratio of $k_{(3)}/k_{(1)}$ and rate constant of corresponding 40 °C is observed as $k = 2.03 \times 10^{-3} \text{ s}^{-1}$. ⁿ2.9 value for PhOCOCl and data from ref. 12. ^oAt 10 °C.

Table 4. Rate constants^a (k/s^{-1}) for solvolyses of isopropenyl chloroformate (**3**) and activation parameters^b

ROCOCl	solvent	T/°C	k/s^{-1}	ΔH^\ddagger	ΔS^\ddagger
				kcal mol ⁻¹	cal mol ⁻¹ K ⁻¹
Me-(1)	water			16.2 ^c	-19 ^c
<i>i</i> -Pr-(2)	water			17.1 ^c	+10 ^c
CH=C(CH ₃)-(b) 3)	water	10	$(1.16 \pm 0.02) \times 10^{-3}$	15.5	-17 ^d
		20	$(2.95 \pm 0.07) \times 10^{-3}$		
		25	4.79×10^{-3e}		
		30	$(7.40 \pm 0.04) \times 10^{-3}$		
		40	$(1.78 \pm 0.05) \times 10^{-2}$		
	ethanol	10	$(2.07 \pm 0.10) \times 10^{-4}$	12.9	-30
		20	$(4.69 \pm 0.07) \times 10^{-4}$		
		30	$(1.02 \pm 0.02) \times 10^{-3}$		
		40	$(2.03 \pm 0.20) \times 10^{-3}$		
		80T-20W ^{e,g}	30		
40	$(5.92 \pm 0.01) \times 10^{-5}$				
50	$(1.30 \pm 0.02) \times 10^{-4}$				

^aDetermined by the identical method with footnote *a* in Table 1. ^bObtained from Eyring plots. ^cQuoted from ref. 17. ^dQuoted from ref. 19a: $\Delta H^\ddagger = 15.0$ kcal mol⁻¹, and $\Delta S^\ddagger = -14$ cal mol⁻¹K⁻¹ for *p*-NO₂PhCOCl, respectively. ^eCalculated using an Arrhenius plot.

(hydrolysis) rate constant of **3** higher than that for **2** $\{[k_{(3)}/k_{(2)}]_{EtOH} = 37.5$ at 40 °C and $[k_{(3)}/k_{(2)}]_{H_2O} = 20.3$ at 25 °C $\}$, *l/m* values (2.97 for **3** and 0.54 for **2**) shown in Table 3 and relatively activation entropy (ΔS^\ddagger) values as described in Table 4.

In studies on the solvolytic reaction for acid chlorides and chloroformates, the value for kinetic solvent isotope effect (KSIE = k_{ROH}/k_{ROD}) provided convincing evidence for a third order reaction (KSIE in methanol ≥ 2.0),^{19a-c,20} based on a general base catalysis (GBC) by a molecule of solvent, as well as a route to mechanistic deduction (≤ 1.2 ;^{21,22} S_N1/S_N2 and ≥ 2.0 ; S_AN mechanism).

As regards solvolysis of **3**, relatively high KSIE values observed in methanol (water) as 2.33 (2.08) support strongly for the validity of a third order mechanism (second order in solvent). and is consistent with previous result predicted from extended GW correlation analyses.

KSIE value and activation parameters for solvolyses of **3** are very similar to those for *p*-nitrobenzoyl chloride (**4**) (with 2.27²²(2.0)²³ value and $\Delta H^\ddagger = 15.0$ kcal mol⁻¹, and $\Delta S^\ddagger = 14$ cal mol⁻¹K⁻¹, respectively), which is known well so far as typical solvolyses (in alcohol-water mixtures) proceeding a third order reaction by a molecule of solvent,^{19a} and are in contrast to those observed for *i*-Pr-(**2**) (favored ionization pathway). Considering differences in solvation²⁴ of aromatic ring and aliphatic group adjacent to reaction center (C=O), our results create further interest in studies of mechanism for solvolyses of **3**.

If one molecule of solvent acts as a nucleophile, and the other molecule acts as a general base, there are four possible third order reaction in binary alcohol-water mixtures, with rate constants k_{ww} , k_{aw} , k_{wa} , and k_{aa} .

Competing third order rate constants for **3** in alcohol-water mixtures; the first letter of the subscript to the rate constant (*k*) refers water (w) or alcohol (a) acting as nucleophile and latter refers to the role solvent as a general base.

Therefore, observed first order rate constants in alcohol-water mixtures are given by equation (3)

$$k_{obs} = k_{aa}[\text{alcohol}]^2 + k_{ww}[\text{water}]^2 + (k_{aw} + k_{wa})[\text{alcohol}][\text{water}] \quad (3)$$

The k_{aa} and the k_{ww} terms can be obtained from the observed first order rate constants in a pure solvent divided by the molar concentration of solvent ($k_{aa} = k_{obs}/[\text{alcohol}]^2$ and $k_{ww} = k_{obs}/[\text{water}]^2$). In the absence of product studies, it is impossible to separate the k_{aw} and the k_{wa} terms from k_{obs} . However, the $(k_{aw} + k_{wa})$ term could be estimated from $k_{obs} - (k_{aa}[\text{alcohol}]^2 + k_{ww}[\text{water}]^2)$.

Third order treatment may be estimated by assuming the solvolytic reaction proceeds by a large stoichiometric effect, which could be accounted for by including an *l*-value in a extended GW treatment.

Contribution from a competing third order rate constants calculated to solvolyses rates (k_{obs}) for **3** in alcohol-water mixtures at 10 °C are reported in Table 5.

As shown in Table 5, the $(k_{aw} + k_{wa})$ terms seemed to be very important for solvolyses of **3** in this work, however, the k_{aa} and the k_{ww} term seemed to be relatively less important.

These results are similar to the results for acid chlorides (RSO₂Cl,^{19b,16} RCOC1^{19a,25}) and chloroformates (ROCOCl)²⁰ so far reported, as the dominancy of the $(k_{aw} + k_{wa})$ term relative to the k_{aa} and k_{ww} term, and these could be attributed to the same way of nucleophilic solvation of reaction site in TS undergoing a competing third order channel and are probably the results reflected relatively high KSIE value with 2.33 (2.08) in methanol (water).

As a whole, these results show the greater contribution from a third order rate constants [k_{ww} , $(k_{aw} + k_{wa})$, and k_{aa}] to solvolyses rate (k_{obs}) for methanol-water mixtures relative to those for ethanol-water mixture, indicating phenomena occurring due to the difference in the phenomena occurring

Table 5. Contribution from third order rate constants to solvolysis rates for Isopropenyl chloroformate (**3**) solvolyses in aqueous methanol (M) and ethanol (E) at 10 °C

% (v/v)	/10 ⁻⁴ s ⁻¹		
	<i>k</i> _{aa} ^a	(<i>k</i> _{aw} + <i>k</i> _{wa}) ^b	<i>k</i> _{ww} ^c
90M	6.02	6.57	0.116
80M	4.75	10.6	0.464
70M	3.64	14.3	1.04
60M	2.68	16.6	1.86
50M	1.86	18.1	2.90
40M	1.19	20.0	4.18
30M	0.669	19.6	5.68
20M	0.297	13.3	7.42
10M	0.0743	2.93	9.40
90E	1.68	2.13	0.116
80E	1.33	2.89	0.464
70E	1.01	3.14	1.04
60E	0.745	4.00	1.86
50E	0.518	4.33	2.90
40E	0.331	5.57	4.18
30E	0.186	8.33	5.68
20E	0.0828	8.29	7.42
10E	0.0207	5.88	9.40

^a*k*_{aa} = *k*_{obs}/[alcohol]² in a pure alcohol. ^bCalculated by rearrangement of eq.(3). ^c*k*_{ww} = *k*_{obs}/[water]² in a pure water.

due to a greater acidity of methanol (pK_a = 15.5),²⁶ which compared with ethanol (pK_a = 16).²⁶ And maximum rate constants (*k* in Table 1) in specific solvent composition for **3** (30%M for methanol and 20%E for ethanol, respectively) are in agreement with maximum contribution from the (*k*_{aw} + *k*_{wa}) term.

Consequently, the results are in accordance with proposed mechanism of general base catalyzed and/or addition elimination for isopropenyl chloroformate (**3**) solvolyses based on prevailing stoichiometric solvation effect.

On the other hand, for TFE (electrophilic)-EtOH (nucleophilic) solvent systems reported as the contrary relation²⁷ between solvent nucleophilicity (N) and solvent ionizing power (N), Application of third order reaction model to solvolysis rate constants (*k*_{obs}) gives us a significant (another) clue for main factor determining rate constants. This model, having possible four third order reactions channel, could be established by the same way as previous described in alcohol-water solvent systems [eq. (3)].

$$k_{\text{obs}} = k_{\text{EE}}[\text{ethanol}]^2 + k_{\text{TT}}[\text{TFE}]^2 + (k_{\text{ET}} + k_{\text{TE}})[\text{ethanol}][\text{TFE}] \quad (4)$$

(E; a molecule of ethanol, T: a molecule of TFE)

In cases where it is established that yields trifluoroethylated products are very low, Equation (4) has been simplified by assuming that the *k*_{TT} term is ignored.

$$k_{\text{obs}} / [\text{ethanol}]^2 = k_{\text{EE}} + (k_{\text{ET}} + k_{\text{TE}}) [\text{TFE}]/[\text{ethanol}] \quad (5)$$

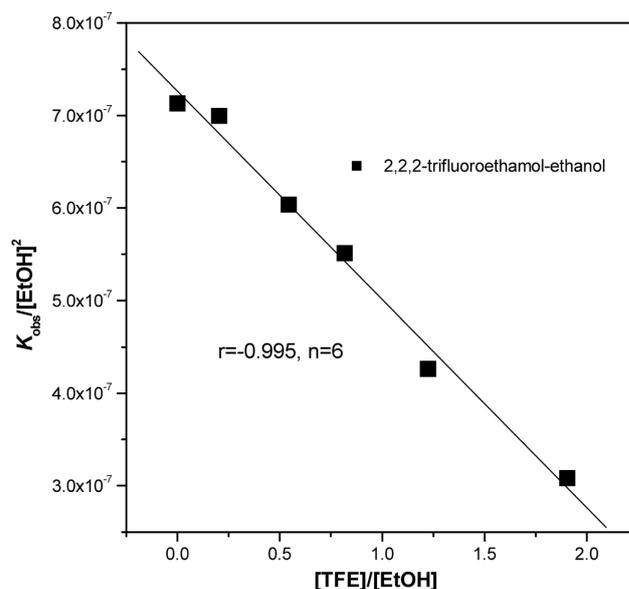


Figure 3. Plots *K*_{obs}/[ethanol]² vs molar ratio of ethanol and TFE for solvolysis of isopropenyl chloroformate (**3**) in TFE-EtOH solvent systems at 10 °C. Plotted using eq. (5); from data for pure solvent *k*_{EE} = 2.07 × 10⁻⁴/(17.14)² = 7.05 × 10⁻⁷ M⁻² s⁻¹ and *k*_{ww} = 1.16 × 10⁻³/(55.5)² = 3.77 × 10⁻⁷ M⁻² s⁻¹; from the correlation line: slope = (-2.25 ± 0.11) × 10⁻⁷ and the intercept (*k*_{EE}) = (7.26 ± 0.12) × 10⁻⁷ M⁻² s⁻¹ (except for 80T-20E solvent point).

A linear relationship with the positive (+) slope between *k*_{obs}/[ethanol]² and the solvent molar ratio [TFE]/[ethanol] was reported for solvolysis rates of acyl chloride,^{5,6} containing an aromatic ring or other electron-withdrawing group (EWG).

In contrast with these, a good linear correlation (*r* = 0.995) with the negative (-) slope = (-2.25 ± 0.11) × 10⁻⁷ and *r* = 0.995 (*n* = 6) for solvolyses of **3** is exhibited in Figure 3, indicating that only the main factor determining the rate constants in TEE-EtOH solvent systems is nucleophilic attack by a molecule of ethanol assisted by other molecule of ethanol (*k*_{EE} term), compared with other solvent, and *k*_{EE} term, corresponding to the intercept, is estimated as a value of (7.26 ± 0.12) × 10⁻⁷ M⁻² s⁻¹, a close consistent with the *k*_{EE} term calculated by *k*_{obs}/[ethanol]² in a pure ethanol (7.05 × 10⁻⁷ M⁻² s⁻¹, see footnote of Fig. 3). A result similar to this for **3** was investigated for solvolyses of *p*-nitrobenzoyl chloride (**4**) (with the negative (-) slope; -4.32 × 10⁻⁶, Table of 5 in ref. 5) at 10 °C. A consistent pattern of solvation effect on reactivity and mechanism of solvolysis is certainly confirmed by these results discussed.

Conclusions

We have now shown that solvent effects on the rates of solvolyses of isopropenyl chloroformate (**3**) are remarkably similar to those for *p*-nitrobenzoyl chloride (**4**) in KSIE, the low sensitivity to solvent ionizing power, high sensitivity to solvent nucleophilicity and *k*_{EE} term as main factor determining rate constants in TFE-EtOH solvent systems.

Solvolytic reactions for **3** fit a third order reaction mechanism, involving attack by a solvent nucleophile assisted by another molecule of solvent acting as a general base, and the rate data are dissected into contributions from four competing reaction channel in alcohol-water solvent systems. Consequently, we can confirm that solvolyses based on predominantly stoichiometric solvation effect relative to medium solvation are proceeding in **3**.

Experimental Section

Materials. Solvents for kinetics in this paper were dried and distilled by standard methods except for dioxane (TCI-GR) used without distillation and aqueous mixtures were prepared by mixing appropriate weights at ambient temperatures, the accurate water contents of 2,2,2-trifluoroethanol-water mixtures, determined by Karl Fischer titration, which is a Model: ORION AF instrument (Hydranal composit 5 K, precision: 0.3% at 1mg H₂O). Isopropenyl chloroformate (**3**) (ACROS organics reagents –AR: 99%) and methanol-*d* (> 99.5 ± > %D) and D₂O (99.9%D), which used Aldrich reagents was used without distillation

Kinetic methods. The rate constants for solvolytic reaction proceeding as pseudo-first type were determined using a general conductimetric method⁵ and calculation of those were performed by the Origin 6.0 program using the Guggenheim equation²⁸ from data monitored automatically.

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References

1. Winstein, S.; Grunwald, E.; Jones, H. W. *J. Am. Chem. Soc.* **1951**, *73*, 2700.
2. Kevill, D. N. In *Advances in Quantitative Structure-Property Relationships*; Chorton, M., Ed.; Jai Press: Greenwich, CT, 1996; Vol 1, p 81.
3. Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1990**, *17*, 121.
4. Kyong, J. B.; Park, B.-C.; Kim, C.-B.; Kevill, D. N. *J. Org. Chem.* **2000**, *65*, 8051, and references therein.
5. Ryu, Z. H.; Lim, G. T.; Bentley, T. W. *Bull. Korean Chem. Soc.* **2003**, *24*, 1293.
6. Oh, Y. H.; Jang, G. G.; Lim, G. T.; Ryu, Z. H. *Bull. Korean Chem. Soc.* **2002**, *23*, 1089.
7. Ryu, Z. H.; Shin, S. H.; Lee, J. P.; Lim, G. T.; Bentley, T. W. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1283.
8. Ryu, Z. H.; Shin, S. H.; Lim, G. T.; Lee, J. P. *Bull. Korean Chem. Soc.* **2004**, *25*, 307.
9. Kevill, D. N.; Kim, C.-B. *J. Org. Chem.* **2005**, *70*, 1490.
10. Number corresponds to number of (v/v)% and letter, M(E) corresponds to methanol (ethanol)-water mixtures.
11. Kevill, D. N.; D'Souza, M. J. *J. Chem. Soc. Perkin Trans. 2* **1997**, 1721.
12. (a) Kevill, D. N.; D'Souza, M. J.; Ren, H. *Can. J. Chem.* **1998**, *76*, 751. (b) Kevill, D. N.; D'Souza, M. J. *J. Phys. Org. Chem.* **2002**, *15*, 881.
13. Kevill, D. N.; Kim, J. C.; Kyong, J. B. *J. Chem. Research(S)* **1999**, 150.
14. Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *98*, 7667.
15. Takeuchi, K.; Ohga, Y.; Ushino, T. *Chem. Lett.* **1996**, 763.
16. (a) Koo, I. S.; Yang, K.; An, S. K.; Lee, C.-K.; Lee, I. *Bull. Korean Chem. Soc.* **2000**, *21*, 1011. (b) Koo, I. S.; Yang, K.; An, S. K.; Lee, J. P.; Lee, I. *Bull. Korean Chem. Soc.* **2004**, *25*, 699.
17. Queen, A. *Can. J. Chem.* **1967**, *45*, 1619.
18. Kyong, J. B.; Kim, Y.-G.; Kim, D. K.; Kevill, D. N. *Bull. Korean Chem. Soc.* **2000**, *21*, 662.
19. (a) Bentley, T. W.; Jones, R. O. *J. Chem. Perkin Trans. 2* **1993**, 2351. (b) Bentley, T. W.; Jones, R. O.; Koo, I. S. *J. Chem. Soc., Perkin Trans. 2* **1994**, 753. (c) Bentley, T. W.; Ebdon, D.; Llewellyn, G.; Abduljabbar, M. H.; Miller, B.; Kevill, D. N. *J. Chem. Soc. Dalton Trans.* **1997**, 3819. (d) Bentley, T. W.; Ebdon, D. N. *J. Phys. Org. Chem.* **2001**, *14*, 759.
20. Koo, I. S.; Yang, K.; Kang, K.; Lee, I.; Bentley, T. W. *J. Chem. Soc. Perkin Trans. 2* **1998**, 1179.
21. Laughton, P. M.; Robertson, R. E. *Solute-Solvent Interaction*; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1969; p 319.
22. Koo, I. S.; Lee, I.; Oh, J.; Yang, Y.; Bentley, T. W. *J. Phys. Org. Chem.* **1993**, *6*, 223.
23. Song, B. C.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8470.
24. Bentley, T. W.; Koo, I. S.; Norman, S. J. *J. Org. Chem.* **1991**, *56*, 1604.
25. Ryu, Z. H.; Ju, C.-K.; Sung, D. D.; Sung, N. C.; Bentley, T. W. *Bull. Korean Chem. Soc.* **2002**, *23*, 123.
26. Sudder, P. H. *Electron Flow in Organic Chemistry*; John Wiley & Sons Inc.: 1992; Composite pKa Chart, p 261.
27. Kaspi, J.; Rappoport, Z. *Tetrahedron Letters* **1977**, *23*, 2035.
28. Guggenheim, E. A. *Philos. Mag.* **1926**, *2*, 538.