

## Rate and Product Studies on the Solvolyses of Allyl Chloroformate

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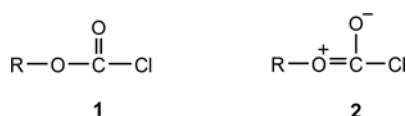
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The solvolysis rate constants of allyl chloroformate ( $\text{CH}_2=\text{CHCH}_2\text{OCOCI}$ , **3**) in 30 different solvents are well correlated with the extended Grunwald-Winstein equation, using the  $N_T$  solvent nucleophilicity scale and  $Y_{Cl}$  solvent ionizing scale, with the sensitivity values of  $0.93 \pm 0.05$  and  $0.41 \pm 0.02$  for  $l$  and  $m$ , respectively. These  $l$  and  $m$  values can be considered to support a  $S_N2$  reaction pathway. The activation enthalpies ( $\Delta H^\ddagger$ ) were 12.5 to 13.4 kcal·mol<sup>-1</sup> and the activation entropies ( $\Delta S^\ddagger$ ) were  $-34.4$  to  $-37.3$  cal·mol<sup>-1</sup>·K<sup>-1</sup>, which is also consistent with the proposed bimolecular reaction mechanism. The solvent kinetic isotope effect (SKIE,  $k_{\text{MeOH}}/k_{\text{MeOD}}$ ) of 2.16 was also in accord with the  $S_N2$  mechanism. The values of product selectivity ( $S$ ) for the solvolyses of **3** in alcohol/water mixtures was 1.3 to 3.9, which is also consistent with the proposed bimolecular reaction mechanism.

**Key Words** : Allyl chloroformate, Extended grunwald-winstein equation,  $S_N2$  mechanism, Solvent kinetic isotope effect, Product selectivity

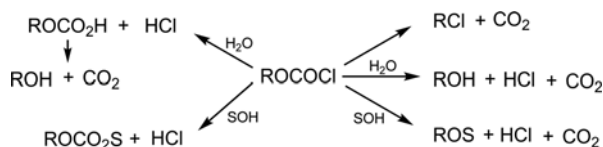
## Introduction

Chloroformate esters ( $\text{ROCOCl}$ , **1**) are known to hydrolyze much slower than other acyl chlorides ( $\text{RCOCl}$ ). An initial-state stabilization through the  $\pi$ -electron resonance **2** has been suggested to be responsible for the reduced reactivity of **1**, whereas a resonance interaction is not possible for  $\text{RCOCl}$ .<sup>1</sup> This resonance effect would be more significant as R in **1** becomes a stronger electron donating group but it would be insignificant as R becomes a stronger 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.<sup>2</sup>



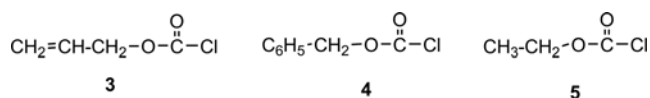
All products could be formed from **1** are presented in Scheme 1. Pathways involving substitutions at the acyl carbon (bimolecular) are shown on the left hand side while pathways involving the direct loss of carbon dioxide accompanying the substitution (unimolecular) on the right hand side.<sup>3</sup>

Studies on the solvolyses of allyl chloroformate (**3**) have



Scheme 1

indicated that an allyl system is similar to a corresponding benzyl system **4** in its solvolytic behavior. However, these

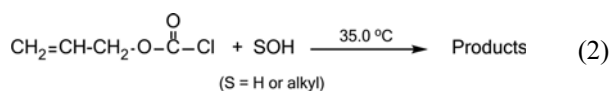


two systems do show some differences, one being that the allyl system is less reactive and more dependent on solvent nucleophilicity.<sup>4</sup> On the other hand, *ab initio* MO calculations<sup>5</sup> of the trigonal bipyramidal five-coordinate transition state (TS) structure at the 6-31++G\* level<sup>6</sup> for the identity exchange of hydride ( $\text{H}^-$ ) have indicated that bond tightness in the TS for the allyl system **3** is similar to that of an ethyl system **5**.

Recently, in a series of work on the application of the extended Grunwald-Winstein equation to the rate constants [Eq. (1)], the magnitudes of  $l$  and  $m$  have proved to be useful for predicting TS structures.<sup>7</sup> In Eq. (1),  $k$  and  $k_o$  represent the rate constants of the solvolysis in a given solvent and a standard solvent (80% ethanol), respectively;  $l$  represents the sensitivity to changes in the solvent nucleophilicity ( $N_T$ ); and  $m$  represents the sensitivity to changes in the solvent ionizing power ( $Y_X$ , for a leaving group X).

$$\log(k/k_o) = lN_T + mY_X \quad (1)$$

In order to gain further understanding of the chloroformate esters mechanism, a kinetic study was conducted on the solvolysis of allyl chloroformate (**3**) in a variety of pure and binary solvents at 35.0 °C [Eq. (2)]. Furthermore, the  $l$  and  $m$  values were determined using the extended Grunwald-Winstein equation<sup>7</sup> [Eq. (1)], together with the enthalpies and entropies of activation, the solvent kinetic isotope effect (SKIE), and product selectivity ( $S$ ).



## Results and Discussion

The rate constants ( $k$ ) for the solvolysis of **3** in 34 pure and binary solvents at 35.0 °C are summarized in Table 1. In this study, the rate constants of the solvolysis represented in

**Table 1.** Rate constants of solvolysis of allyl chloroformate<sup>a</sup> (**3**) 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 <sup>b</sup>	$10^4 k$ (s <sup>-1</sup> ) <sup>c</sup>	$N_T$ <sup>d</sup>	$Y_{Cl}$ <sup>d</sup>
100% EtOH	0.775 ± 0.004	0.37	-2.52
90% EtOH	2.82 ± 0.05	0.16	-0.94
80% EtOH	3.95 ± 0.03	0.0	0.0
70% EtOH	4.71 ± 0.03	-0.20	0.78
60% EtOH	5.97 ± 0.02	-0.38	1.38
50% EtOH	7.41 ± 0.04	-0.58	2.02
40% EtOH	9.37 ± 0.03	-0.74	2.75
20% EtOH	12.1 ± 0.3	-1.16	4.09
100% MeOH	3.78 ± 0.02	0.17	-1.20
90% MeOH	5.13 ± 0.05	-0.01	-0.20
80% MeOH	8.71 ± 0.04	-0.06	0.67
70% MeOH	12.3 ± 0.5	-0.40	1.46
60% MeOH	14.1 ± 0.4	-0.54	2.07
50% MeOH	19.2 ± 0.4	-0.75	2.70
40% MeOH	23.4 ± 0.7	-0.87	3.25
20% MeOH	29.5 ± 0.6	-1.23	4.10
90% Acetone	0.234 ± 0.004	-0.35	-2.39
80% Acetone	0.607 ± 0.003	-0.37	-0.83
70% Acetone	1.25 ± 0.03	-0.42	0.17
60% Acetone	2.04 ± 0.05	-0.52	1.00
50% Acetone	2.74 ± 0.04	-0.70	1.73
40% Acetone	4.42 ± 0.04	-0.83	2.46
30% Acetone	7.21 ± 0.03	-0.96	3.21
20% Acetone	9.55 ± 0.05	-1.11	3.77
90% TFE <sup>e</sup>	0.195 ± 0.004	-2.55	2.85
80% TFE	0.427 ± 0.005	-2.19	2.90
70% TFE	0.813 ± 0.004	-1.98	2.96
50% TFE	1.28 ± 0.03	-1.73	3.16
90% HFIP <sup>e</sup>	0.0835 ± 0.0005	-3.84	4.31
70% HFIP	0.503 ± 0.003	-2.94	3.83
50% HFIP	1.06 ± 0.04	-2.49	3.80
80T-20E <sup>f</sup>	0.153 ± 0.003	-1.76	1.89
60T-40E	0.242 ± 0.004	-0.94	0.63
40T-60E	0.411 ± 0.002	-0.34	-0.48
20T-80E	0.877 ± 0.005	0.08	-1.42

<sup>a</sup>Unless otherwise indicated, a 1.0 mol dm<sup>-3</sup> solution of the substrate in the indicated solvent, containing 0.1% CH<sub>3</sub>CN was used for this study. <sup>b</sup>On a volume-volume content at 25.0 °C, and the other component is water. <sup>c</sup>With associated standard deviations. <sup>d</sup>Values from ref. 7. <sup>e</sup>The solvent is prepared on a weight-weight basis at 25.0 °C, and the other component is water. TFE: 2,2,2-trifluoroethanol, HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol. <sup>f</sup>TFE-ethanol mixtures.

Eq. (2) were measured using an automatic conductivity apparatus. In order to promote a rapid dissolution in the solvent, the substrate was added as a small volume of a concentrated stock solution of 0.1% acetonitrile. In most solvents, the reactions proceeded rapidly, which enabled the responses to be recorded as a function of time.<sup>8</sup>

The rate constants increased as the amount of water in the binary solvent systems was increased as shown in Table 1. A faster solvolysis reaction was observed in the nucleophilic solvent systems whereas a slower reaction was observed in the electrophilic solvent systems. This phenomenon supports that the solvolysis of **3** is dominated by a bimolecular reaction mechanism.<sup>7</sup>

The rate constant for the ethanolsolysis of **3** measured in this study was  $3.88 \times 10^{-5} \text{ s}^{-1}$  at 25.0 °C (Table 2), which was smaller than that previously reported for the benzyl chloroformate (**4**)<sup>9</sup> ( $k = 5.16 \times 10^{-5} \text{ s}^{-1}$  at 25.0 °C). This suggests that the electron-withdrawing power of the allyl group (CH<sub>2</sub>=CHCH<sub>2</sub>-) is weaker than that of the benzyl group (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-), and therefore it would be less favorable for a nucleophilic attack at the electron-deficient carbonyl carbon.

The activation parameters ( $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) calculated from the  $k$  values at four different temperatures for the solvolysis of **3** in pure EtOH, 80% EtOH, and pure MeOH are shown in Table 2. The values of  $\Delta H^\ddagger$  were relatively low (12.5 to 13.4 kcal·mol<sup>-1</sup>) and the values of  $\Delta S^\ddagger$  were largely negative (-34.4 to -37.3 cal·mol<sup>-1</sup>·K<sup>-1</sup>), which are within the range of the previously reported results for a normal S<sub>N</sub>2 reaction.<sup>10</sup> In the deuterated methanol (MeOD), a SKIE ( $k_{\text{MeOH}}/k_{\text{MeOD}}$ ) of  $2.16 \pm 0.04$  was observed at 35.0 °C. This value is within the range of 2.14-2.35, which was reported for the corresponding methanolyses of phenyl chloroformate,<sup>10</sup> 9-fluorenyl chloroformate,<sup>11</sup> and 2,2,2-trichloro-1,1-dimethylethyl chloroformate<sup>12</sup> and in which the reactions are believed to be a S<sub>N</sub>2 reaction in character<sup>13</sup> (Table 3).

The magnitudes of  $l$  and  $m$  in the extended Grunwald-

**Table 2.** Rate constants and activation parameters for the solvolysis of allyl chloroformate<sup>a</sup> (**3**) at various temperatures

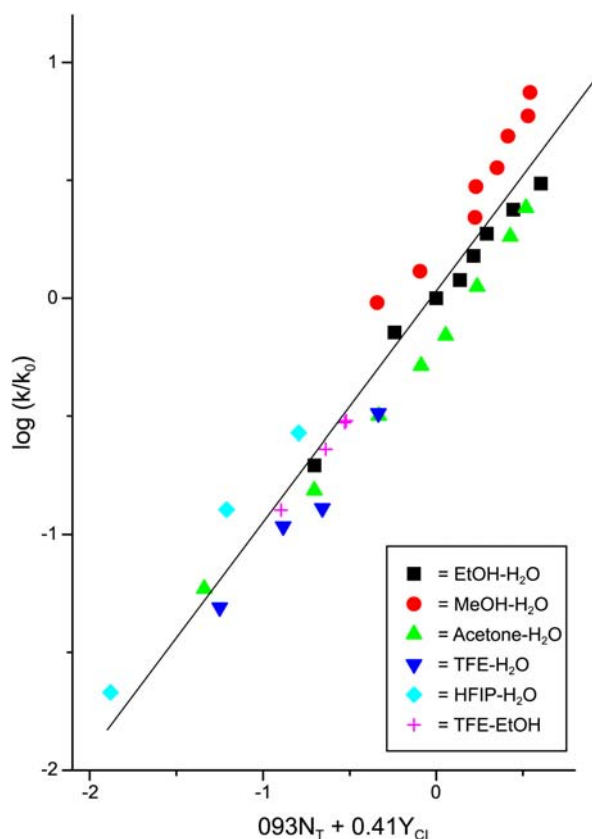
Solvent	Temp. (°C)	$10^4 k$ (s <sup>-1</sup> ) <sup>b</sup>	$\Delta H^\ddagger$ (kcal·mol <sup>-1</sup> ) <sup>c</sup>	$-\Delta S^\ddagger$ (cal·mol <sup>-1</sup> ·K <sup>-1</sup> ) <sup>c</sup>
100% EtOH	25.0	0.388 ± 0.002	12.6 ± 0.4	36.8 ± 1.4
	35.0	0.775 ± 0.004		
	45.0	1.55 ± 0.05		
	55.0	3.10 ± 0.03		
80% EtOH <sup>d</sup>	25.0	2.01 ± 0.05	12.5 ± 0.5	37.3 ± 1.7
	35.0	3.95 ± 0.03		
	45.0	7.78 ± 0.04		
	55.0	15.6 ± 0.3		
100% MeOH	25.0	1.77 ± 0.03	13.4 ± 0.6	34.4 ± 1.9
	35.0	3.78 ± 0.02		
	45.0	7.57 ± 0.03		
	55.0	16.2 ± 0.4		

<sup>a</sup>A 1.0 mol dm<sup>-3</sup> solution of the substrate in each solvent, also containing 0.1% CH<sub>3</sub>CN. <sup>b</sup>Average of three or more runs, with standard deviation. <sup>c</sup>The activation parameters are accompanied by the standard error. <sup>d</sup>On a volume-volume content at 25.0 °C, and the other component is water.

**Table 3.** Rate constants and solvent kinetic isotope effects (SKIEs) for solvolysis of various substrates in methanol

Substrate	Temp. °C	$k_{\text{CH}_3\text{OH}}$ (s <sup>-1</sup> ) <sup>a</sup>	$k_{\text{CH}_3\text{OD}}$ (s <sup>-1</sup> ) <sup>a</sup>	$k_{\text{CH}_3\text{OH}}/k_{\text{CH}_3\text{OD}}$ <sup>b</sup>
C <sub>6</sub> H <sub>5</sub> OCOCl <sup>c</sup>	25.0	$7.93(\pm 0.03) \times 10^{-3}$	$2.95(\pm 0.03) \times 10^{-3}$	$2.35 \pm 0.03$
9-Fluorenyl-OCOCl <sup>d</sup>	45.0	$13.8(\pm 0.2) \times 10^{-4}$	$6.27(\pm 0.03) \times 10^{-4}$	$2.20 \pm 0.03$
Cl <sub>3</sub> CC(CH <sub>3</sub> ) <sub>2</sub> OCOCl <sup>e</sup>	35.0	$17.8(\pm 0.4) \times 10^{-4}$	$7.85(\pm 0.04) \times 10^{-4}$	$2.14 \pm 0.04$
CH <sub>2</sub> =CHCH <sub>2</sub> OCOCl	35.0	$3.78(\pm 0.02) \times 10^{-4}$	$1.75(\pm 0.03) \times 10^{-4}$	$2.16 \pm 0.03$

<sup>a</sup>Standard deviation. <sup>b</sup>Standard error from ref. 14. <sup>c</sup>Ref. 10. <sup>d</sup>Ref. 11. <sup>e</sup>Ref. 12.

**Figure 1.** Plots of  $\log(k/k_0)$  for the solvolysis of allyl chloroformate (**3**) at 35.0 °C against  $(0.93 N_T + 0.41 Y_{Cl})$ .

Winstein equation [Eq. (1)] are used as the indicators to determine whether a nucleophilic substitution reaction proceeds through a unimolecular ( $l \approx 0$  and  $m \approx 1$ ) or a bimolecular reaction ( $l \approx 1.0$  and  $m \approx 0.5$ ).<sup>9,11,12</sup>

The application of the extended Grunwald-Winstein equation [Eq. (1)]<sup>15,16</sup> to the rate constants of **3** (from Table 1) leads to a moderately good correlation with  $N_T$  and  $Y_{Cl}$ . For 34 solvents,  $l$  and  $m$  values were respectively  $0.98 \pm 0.06$  and  $0.44 \pm 0.03$  with a correlation coefficient ( $R$ ) of 0.946. On excluding data concerning TFE-ethanol mixture, a better correlation coefficient ( $R = 0.964$ ) was obtained with the  $l$  value of  $0.93 \pm 0.05$  and the  $m$  value of  $0.41 \pm 0.02$ . In the correlations of other solvolyses in the previous studies containing TFE-ethanol, solvent systems usually lie below the correlation line.<sup>15</sup> The sensitivity values ( $l$  and  $m$ ) for **3** as well as those for related substrates from the relevant literature are presented in Table 4.

The  $l$  value of 0.93 and  $m$  value of 0.41 for **3** were smaller

**Table 4.** Extended Grunwald-Winstein correlations of the kinetics of solvolytic displacement of chloride

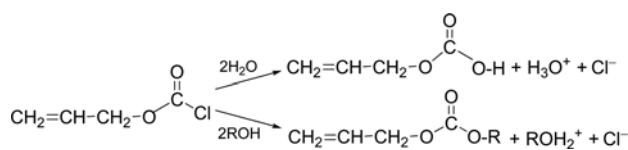
Substrate	$n^a$	$l^b$	$m^b$	$l/m$	$R^c$
1-AdOCOCl <sup>d</sup>	15	~0	$0.47 \pm 0.04$	~0	0.985
2-AdOCOCl <sup>d</sup>	19	~0	$0.47 \pm 0.03$	~0	0.970
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCOCl <sup>e</sup>	11	$0.25 \pm 0.05$	$0.66 \pm 0.06$	0.28	0.976
<i>i</i> -PrOCOCl <sup>f</sup>	20	$0.28 \pm 0.05$	$0.52 \pm 0.03$	0.54	0.979
CH <sub>2</sub> =CHCH <sub>2</sub> OCOCl	30	$0.93 \pm 0.05$	$0.41 \pm 0.02$	2.3	0.964
9-Fluorenyl-OCOCl <sup>g</sup>	30	$0.95 \pm 0.07$	$0.38 \pm 0.04$	2.5	0.941
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PSCl <sup>h</sup>	25	$1.00 \pm 0.04$	$0.64 \pm 0.03$	1.6	0.983
(CH <sub>3</sub> ) <sub>2</sub> (C <sub>3</sub> O <sub>2</sub> )POCl <sup>i</sup>	27	$1.03 \pm 0.05$	$0.43 \pm 0.02$	2.4	0.974
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl <sup>j</sup>	37	$1.10 \pm 0.17$	$0.61 \pm 0.04$	1.8	0.959
((CH <sub>3</sub> ) <sub>2</sub> N) <sub>2</sub> POCl <sup>k</sup>	27	$1.14 \pm 0.05$	$0.63 \pm 0.03$	1.8	0.982
(CH <sub>3</sub> ) <sub>2</sub> PSCl <sup>l</sup>	28	$1.16 \pm 0.08$	$0.55 \pm 0.03$	2.1	0.966
(CH <sub>3</sub> ) <sub>2</sub> NSO <sub>2</sub> Cl <sup>l</sup>	26	$1.17 \pm 0.06$	$0.70 \pm 0.04$	1.7	0.975
CH <sub>3</sub> SO <sub>2</sub> Cl <sup>m</sup>	43	$1.20 \pm 0.05$	$0.52 \pm 0.03$	2.3	0.969
C <sub>2</sub> H <sub>5</sub> OCOCl <sup>f</sup>	28	$1.56 \pm 0.09$	$0.55 \pm 0.03$	2.8	0.967
CH <sub>3</sub> OCOCl <sup>f</sup>	19	$1.59 \pm 0.09$	$0.58 \pm 0.05$	2.7	0.977
<i>n</i> -OctOCOCl <sup>f</sup>	19	$1.67 \pm 0.07$	$0.76 \pm 0.03$	2.2	0.988
C <sub>6</sub> H <sub>5</sub> OCOCl <sup>e</sup>	21	$1.68 \pm 0.10$	$0.57 \pm 0.06$	3.0	0.973

<sup>a</sup>Number of solvents. <sup>b</sup>From Eq. (1) and with an associated standard error. <sup>c</sup>Multiple correlation coefficient. <sup>d</sup>Ref. 16. <sup>e</sup>Ref. 10. <sup>f</sup>Ref. 17. <sup>g</sup>Ref. 11. <sup>h</sup>Ref. 18. <sup>i</sup>Ref. 19. <sup>j</sup>Ref. 20. <sup>k</sup>Ref. 15. <sup>l</sup>Ref. 21. <sup>m</sup>Ref. 22.

than those reported for the reactions that advanced through an addition-elimination mechanism ( $l = 1.56$ - $1.68$  and  $m = 0.55$ - $0.76$ ), but similar to those reported for the bimolecular solvolyses of other substrates (Table 4). This suggests that there is an S<sub>N</sub>2 mechanism involving a nucleophilic attack by the solvent at the carbonyl carbon atom of **3**. The solvolysis of **3**, where the bond making ( $l = 0.93$ ), is more progressed than the bond breaking ( $m = 0.41$ ) in the TS.<sup>17</sup>

The lower  $m$  value ( $m = 0.41$ ) for the solvolysis of **3**, compared with that of phenyl chloroformate ( $m = 0.57$ ),<sup>10</sup> methyl chloroformate ( $m = 0.58$ ),<sup>17</sup> and ethyl chloroformate ( $m = 0.55$ ),<sup>17</sup> would reflect a reduced need for the solvation of the developing negative charge on the carbonyl oxygen.

The  $l$  to  $m$  ratios have also been suggested as a useful mechanistic criterion.<sup>10-15</sup> For the solvolysis of **3**, the  $l/m$  value was calculated to be 2.3, which is similar to those of *N,N*-dimethyl sulfamoyl chloride ((CH<sub>3</sub>)<sub>2</sub>NSO<sub>2</sub>Cl),<sup>17</sup> methylsulfonyl chloride (CH<sub>3</sub>SO<sub>2</sub>Cl),<sup>22</sup> dimethyl thiophosphorochloridate ((CH<sub>3</sub>O)<sub>2</sub>PSCl),<sup>21</sup> and *N,N,N',N'*-tetramethyldi-amido-phosphorochloridate ((CH<sub>3</sub>)<sub>2</sub>N)<sub>2</sub>POCl,<sup>15</sup> to suggest the existence of a S<sub>N</sub>2 mechanism. The  $l/m$  value for the solvolysis of **3** ( $l/m = 2.3$ ) is more similar to that of the corresponding reactions of ethyl chloroformate ( $l/m = 2.8$ ,



Scheme 2

5)<sup>17</sup> than that of benzyl chloroformate ( $l/m = 0.28, 4$ ).<sup>10</sup>

The  $k_{80\% \text{ EtOH}}/k_{100\% \text{ EtOH}}$  ratio has also been suggested as a useful mechanistic criterion.<sup>10-15</sup> The  $k_{80\% \text{ EtOH}}/k_{100\% \text{ EtOH}}$  values of 95 to 320 are considered to represent a  $S_N1$  reaction or an ionization pathway.<sup>7a,d</sup> On the contrary, less sensitive  $k_{80\% \text{ EtOH}}/k_{100\% \text{ EtOH}}$  values were reported for the proposed  $S_N2$  reaction due to the solvent ionizing power: the solvolyses of methyl chloroformate (4.0),<sup>17</sup> ethyl chloroformate (3.2),<sup>17</sup> and *p*-methylbenzoyl chloride (5.3).<sup>13</sup> Therefore, the  $k_{80\% \text{ EtOH}}/k_{100\% \text{ EtOH}}$  value of 5.1 for the solvolysis of **3** is similar to those of the three substrates, that suppose the mechanism of  $S_N2$  reaction.

The product formation of **3** through reactions with water produces two equivalents of strong acid and the reaction with an alcohol produces only one equivalent of strong acid. If a water-alcohol solvent is used, the equation, as presented in Scheme 2, is simplified in that the second solvent molecule, which is used to extract the proton from the molecule serving as the nucleophile, could be either water or alcohol. Furthermore, the amounts of each of the two protonated solvent species shown are determined *via* a rapid equilibration within the mixed solvent.

The partitioning ratio ([ester]/[acid]) is used in conjunction with the molar composition ratio for the solvent involved ( $[\text{H}_2\text{O}]/[\text{ROH}]$ ) in order to calculate the selectivity value ( $S$ ), defined as Eq. (3). The values for the percentages of reactions proceeding with ester formation

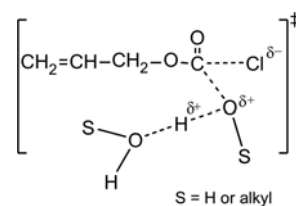
$$S = \frac{[\text{Ester in product}]}{[\text{Acid in product}]} \times \frac{[\text{H}_2\text{O in solvent}]}{[\text{ROH in solvent}]} \quad (3)$$

(x%) for solvolyses of **3** at 35.0 °C in the binary mixtures of water with ethanol or methanol are reported in Table 5. The product ratios ( $x/100 - x$ ) were then used in Eq. (3) to provide the  $S$  values, which are also presented in Table 5.

**Table 5.** Selectivity values ( $S$ )<sup>a</sup> for solvolyses of allyl chloroformate (**3**) at 35.0 °C in the binary mixtures of water with ethanol or methanol

Alcohol % (v/v)	EtOH-H <sub>2</sub> O		MeOH-H <sub>2</sub> O	
	% Ester <sup>b</sup>	$S$	% Ester <sup>b</sup>	$S$
90	80.0	1.3	86.4	1.6
80	63.4	1.4	80.6	1.8
70	56.6	1.8	67.7	2.0
60	47.9	2.2	64.4	2.6
40	36.9	2.8	51.7	3.6
20	19.7	3.2	30.8	3.9

<sup>a</sup>As defined in Eq. (3). <sup>b</sup>Molar percentage of ester formed in competition with the acid; average deviation  $\pm 3\%$ .



Scheme 3

The product selectivities ( $S$ , Table 5) reveal that for aqueous ethanol and methanol mixtures the selectivity increases with increases in the water content. Thus, the reactivity-selectivity principle (RSP)<sup>23</sup> is not followed in ethanol and methanol mixtures.

The greater value of  $S$  in the more aqueous media for **3** is a strong indication that the role of alcohol as a nucleophile is important while the effect of the ionizing power is insignificant in the product-determining step of the reaction of **3**. Similar selectivity changes have been shown to be typical for a general bimolecular reaction mechanism channel in aqueous alcohol media.<sup>24</sup>

## Conclusions

The application of the extended Grunwald-Winstein equation to the solvolysis of **3** led to a  $l$  value of 0.93 and an  $m$  value of 0.41. 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 4). Therefore, it can be concluded that the solvolysis of **3** proceeds through an  $S_N2$  reaction (Scheme 3), in which the bond making might be more progressed than the bond breaking considering the bases of the magnitudes of  $l$  and  $m$ . This conclusion can be further supported by the reasonable activation parameters (*i.e.*, relatively small  $\Delta H^\ddagger$  and large negative  $\Delta S^\ddagger$ ) and the solvent kinetic isotope effect (2.16). The selectivity values ( $\Delta S^\ddagger = 1.3-3.9$ ) obtained in the binary solvents were also consistent with the proposed mechanism.

## Experimental

The solvents were purified as previously described.<sup>13,22</sup> The allyl chloroformate (**3**, Aldrich, 98%) was used as received. The kinetic experiments were performed by allowing a conductivity cell containing 12.5 mL of solvent to equilibrate, while stirring in a constant-temperature water bath. Then, a 12  $\mu\text{L}$  portion of a 1.0 mol  $\text{dm}^{-3}$  stock solution of **3** in acetonitrile was added. The monitoring of the conductivity increased with time and the rate constant calculations were conducted as previously reported.<sup>13,22</sup> Multiple regression analyses were performed using commercially available packages.<sup>13,22</sup>

For the solvolyses of **3**, the infinity titers could be used to obtain the fractions of reaction proceeding to ester and to acid in water-alcohol mixtures.<sup>25</sup> A 0.43 M solution of the substrate in acetonitrile was prepared and 0.30 mL was added to 20 mL of the binary solvent mixture under investi-

gation. To standardize the measurements, each series of compositions of an aqueous alcohol mixtures was accompanied by solvolysis in 60% acetone (2 equivalents of acid produced). All determinations were in duplicate and 5.0 mL portions were titrated in the usual manner<sup>7g,21,25</sup> at 10, 15 and 20 half lives. Also the product selectivities (*S*) were calculated using Eq. (3).

The indicator and solution for titration were prepared by used the following methods. The solution of lacmoid (indicator): 0.004 g of lacmoid was added to 1 L distilled acetone and then the solution was stirred for 24 h. Some dilute nitric acid was added to the distilled acetone. A 25 mL sample of the mixture was removed and one drop of sodium methoxide in MeOH was added to the sample to try and bring about a color change (blue to red). If no color change was visible, more dilute nitric acid was added to the initial distilled acetone solution until a sample of the mixture produced a color change. It was then stirred for 12 h.

**Standardization of Solution of Sodium Methoxide.** A 250 mL solution of sodium methoxide was made by placing 0.5 g sodium methoxide in a 250 mL volumetric flask and diluted to the line. Three solutions of potassium hydrogen phthalate (KHP) were made by putting 0.0195 g, 0.0188 g, and 0.0196 g KHP into each and adding 25 mL water. Each KHP was dried for 2 h at 120 °C to remove any absorbed moisture. Each flask was titrated with the solution of sodium methoxide. The average factor was 0.9434 which was multiplied by the theoretical sodium methoxide concentration ( $4.72 \times 10^{-2}$  M: real concentration of sodium methoxide).

**Second Standardization of Solution of Hydrochloric Acid by the Standardized Solution of Sodium Methoxide.** 1030  $\mu$ L of concentrated hydrochloric acid (37.2%) diluted with 250 mL water was stirred until completely mixed and then was set aside for 12 h of titrations. A solution of sodium methoxide was poured into a burette. 2 mL of the hydrochloric acid was placed in each of the three erlenmeyer flasks with 25 mL water, respectively and then 2-3 drops of phenolphthalein indicator was added to the solution of hydrochloric acid.

**Standardization of Solution of Sodium Methoxide in Methanol by the Standardized Solution of Hydrochloric Acid.** Methanol was added to the sodium methoxide/methanol mixture to make 1 L and then stirred for 5 minutes. This solution was then placed in a 1 L bottle for the automatic titration instrument. 1 mL of  $4.76 \times 10^{-2}$  M hydrochloric acid and 25 mL of resorcinol blue indicator was placed in an erlenmeyer flask and stirred. A solution of sodium hydroxide obtained from the automatic titrations for the three trials were 12.630, 12.516 and 12.727 mL.

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