JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15:** 758–764

Correlation of the rates of solvolyses of cinnamyl chloride

In Sun Koo,[1]* Sun Kyoung An,[1] Kiyull Yang,[1] Ikchoon Lee[2] and T. William Bentley[3]

[1]Department of Chemical Education and Research Institute of Natural Science, Gyeongsang National University, Chinju 660-701, Korea
[2]Department of Chemistry, Inha University, Incheon 402-751, Korea
[3]Department of Chemistry, University of Wales, Swansea, Singleton Park, Swansea SA2 8PP, UK

Received 15 November 2001; revised 26 June 2002; accepted 5 July 2002

ABSTRACT: Solvolytic rate constants (*k*) at 25 °C are reported for solvolyses of cinnamyl chloride (**1**) in binary mixtures of water with acetone, ethanol, methanol, methanol-*d* and 2,2,2-trifluoroethanol (TFE), and also in TFE–ethanol mixtures; product selectivities (*S*) are reported for aqueous ethanol and methanol: *S* = [ether product]/[alcohol product] × [water]/[alcohol solvent]. A good correlation observed between log *k* and the parameter Y_{Cl} (solvent ionizing power) is improved only slightly by additional parameters (*N* for solvent nucleophilicity and/or *I*, an aromatic ring parameter). Rate ratios in solvents of the same Y_{Cl} value but different nucleophilicities provide measures of the minimum extent of nucleophilic solvent assistance, and the value of 1.48 for $[k_{40EW}/k_{97TFE}]_Y$ (EW = ethanol–water) is consistent with an essentially S_N1 reaction mechanism. A linear relationship between 1/*S* and molar ratio of solvent was derived theoretically and validated experimentally for solvolyses of the above substrate from water up to 75% alcohol–water. The dependence of *S* on solvent composition and the absence of rate depression in the presence of added chloride anions are explained by product formation via a contact ion pair. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: cinnamyl chloride; kinetics; solvolysis; selectivity

INTRODUCTION

The Grunwald–Winstein (GW) equation [Eqn. (1)][1–5] has often been applied to the correlation of solvolysis rates; in Eqn. (1), *k* is the rate constant for solvolysis in any solvent relative to 80% ethanol–water (k_0), *m* is the sensitivity of the substrate to the solvent ionizing power (*Y*) and *c* is a residual intercept term. Further developments include modified *Y* values[6] and the incorporation of a term for solvent nucleophilicity [*N*, extended GW equation, Eqn. (2)].[5–8]

$$\log(k/k_0) = mY + c \qquad (1)$$

$$\log(k/k_0) = mY + lN \qquad (2)$$

Dispersion (separate correlation lines observed for various binary mixtures) was documented[1–5] in earlier treatments, and it is now recognized that dispersion can be associated with many factors, including leaving group effects,[4,6] solvent nucleophilicity,[7,8] aromatic ring solvation,[9–11] solvation effects adjacent to the reaction site[12] and competing reactions.[13–15] In general, leaving group effects are minimized by comparing solvolyses with the same leaving group, and dispersion effects in unimolecular (S_N1) solvolyses[1–4] are smaller than the effects of solvent nucleophilicity in bimolecular (S_N2) solvolyses.[5–8]

Kevill *et al.* recently showed that, since dispersion often follows a consistent pattern, an aromatic ring parameter (*I*) and the appropriate sensitivity (*h*) may be added to Eqns (1) and (2) to give Eqns (3) and (4), respectively;[16–19] one aim of our work was to continue investigations using Eqns (1)–(4).

$$\log(k/k_0) = mY + hI + c \qquad (3)$$

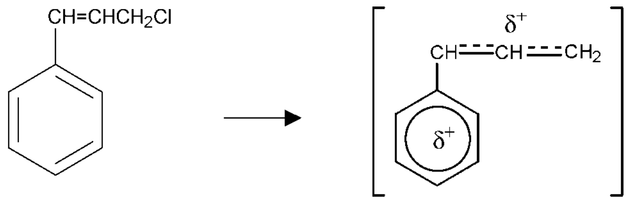
$$\log(k/k_0) = mY + lN + hI + c \qquad (4)$$

Solvolytic reactions in alcohol–water mixtures lead to alcohol and ether products from which selectivities can be calculated using Eqn. (5):[10,20–24]

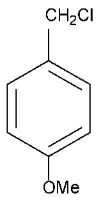
$$S = [\text{ether product}]/[\text{alcohol product}] \times [\text{water}]/[\text{alcohol solvent}] \qquad (5)$$

Nucleophilic attack may occur on ‘free’ carbocations, solvent-separated ion pairs, contact ion pairs or neutral substrates, and the solvent dependence of *S* may be due to changes in the nature of the intermediate leading to product.[24,25] An alternative explanation, involving general base-catalysed nucleophilic attack on carbocations, accounts for the linear relationship between 1/*S* and the alcohol/water molar ratio for S_N1 solvolyses of *p*-methoxybenzyl and diphenylmethyl chlorides.[24]

**Correspondence to:* I. S. Koo, Department of Chemical Education, Gyeongsang National University, Chinju 660–701, Korea.
E-mail: iskoo@nongae.gsnu.ac.kr
Contract/grant sponsor: Korea Science and Engineering Foundation; *Contract/grant number:* KOSEF 2001-1-12300-008-2.



1 $\quad$ **1^+**



2

Another aim of our work was to test whether there is a linear relationship between $1/S$ and the alcohol/water molar ratio, as predicted by Eqn. (6), for the product-determining step of S_N1 reactions of carbocations.

$$1/S = (k_{wa}/k_{aw})([\text{alcohol solvent}]/[\text{water}]) + k_{ww}/k_{aw} \qquad (6)$$

Suitable substrates on which to test Eqn. (6) are those which react only by substitution pathways via carbocations.[24] Also, the substrates should permit rapid mixing in highly aqueous mixtures, and should not be so reactive that their solvolyses are interfacial.[10] As a suitable substrate, we chose cinnamyl chloride (**1**), which is expected to react by an S_N1 pathway in view of the stable cationic form, $\mathbf{1}^+$.

As the positive charge on the cation $\mathbf{1}^+$ is highly delocalized, and **1** contains carbon atoms attached to both alkene and aromatic ring carbon atoms, applications of the GW Eqn. (1), the extended GW Eqn. (2) and the aromatic ring parameter [Eqns (3) and (4)] to solvolyses of **1** will extend the scope of previous work.[9–12,16–19]

RESULTS

Rate constants for solvolyses of **1** in aqueous binary mixtures of acetone, ethanol, methanol, methanol-*d*, water, 2,2,2-trifluoroethanol (TFE)–water (%, w/w) and TFE–ethanol (%, v/v) at 25.0 °C are reported in Tables 1 and 2, and salt effects for $NaClO_4$, NaCl, and LiCl in 90% methanol–water are given in Table 3. Results at various temperatures are given in Table 4 along with the corresponding Arrhenius parameters. Selectivity data, obtained from product analyses as soon as possible after completion of 10 half-lives of reaction,[24] are given in Table 5 for solvolyses of **1** in ethanol–water and methanol–water mixtures at 25.0 °C.

Table 1. Rate constants for solvolyses of cinnamyl chloride (**1**) in aqueous binary mixtures at 25 °C[a]

	$k \times 10^3$ (s^{-1})		
% (v/v)	MeOH	EtOH	Acetone
100	0.00851[b]	0.000839	
90	0.0435	0.00970	
80	0.225	0.0473	0.00215
70	0.722	0.161	0.0144
60	2.28	0.499	0.0770
50	6.31	1.69	0.414
40	16.5	7.46	1.90
30	35.8	22.8	8.81
20	72.0	66.7	32.7
10	112	106	61.0
H_2O	149	149	149

[a] Determined conductometrically at least in duplicate; typical error ±3%.
[b] Solvolyses in MeOD give $k = 7.62\ (\pm 0.10) \times 10^{-6}$ s^{-1}, giving a kinetic solvent isotope effect of 1.11.

DISCUSSION

Kinetic data

For binary solvents having the same % (v/v) water, the rate constants (Table 1) increase in the order acetone–H_2O <ethanol–H_2O <methanol–H_2O. The rates increase appreciably as the water content of a mixture increases; thus the rate is higher in solvents with higher ionizing power, *Y*. First-order rate constants for solvolyses of **1** vary 2×10^5-fold in alcohol–water mixtures. These results are very similar to those of solvolytic reactions of *p*-methoxybenzoyl chloride[14,26,27] and of *p*-methoxybenzyl chloride (**2**):[26,28] see Fig. 1, which shows that the primary substrate **2** is a very good similarity model (Y_{sim}[12]) for rate constants for solvolyses of **1**, including TFE-rich mixtures. Rate constants for solvolyses of **2** also correlate well with Y_{BnCl}, but with deviations for 100% TFE and other TFE-rich solvent mixtures.[28] The

Table 2. Rate constants for solvolyses of cinnamyl chloride (**1**) in 2,2,2-trifluoroethanol binary mixtures at 25 °C[a]

TFE–H_2O		TFE–EtOH	
% (w/w)	$k \times 10^3$ (s^{-1})	% v/v	$k \times 10^3$ (s^{-1})
100TFE	4.70	80TFE-20EtOH	0.848
97TFE-3H_2O	5.05[b]	60TFE-40EtOH	0.104
90TFE-10H_2O	5.90	40TFE-60EtOH	0.0191
70TFE-30H_2O	12.0	20TFE-80EtOH	0.00353
50TFE-50H_2O	25.6		

[a] Determined conductometrically at least in duplicate; typical error ±3%.
[b] $k_{40EW}/k_{97TFE} = 1.48$ (k_{40EW} taken from Table 1).

Table 3. Rate constants for solvolyses of cinnamyl chloride (**1**) in salt solution in 90% methanol–10% water binary mixtures at 25 °C[a]

Added salt	$k \times 10^5$ (s^{-1})
0.1 M $NaClO_4$	4.51
0.1 M NaCl	4.56
1.0 M LiCl	5.33
1.0 M $NaClO_4$	5.12

[a] Determined titrimetrically at least in duplicate; typical error ±3%.

Table 4. Additional rate constants for solvolyses of cinnamyl chloride (**1**) in aqueous alcohol mixtures and activation parameters calculated using data at 35 and 45 °C

Solvent	*T* (°C)	*k* (s^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})[a]	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})[a]
50% EtOH	35	5.42×10^{-3}	19.3	−6.5
50% EtOH	45	1.41×10^{-2}		
30% EtOH	35	6.06×10^{-2}	16.1	−11.9
30% EtOH	45	1.43×10^{-1}		
50% MeOH	35	1.80×10^{-2}	17.0	−11.4
50% MeOH	45	4.36×10^{-2}		
30% MeOH	35	1.03×10^{-1}	17.2	−7.4
30% MeOH	45	2.54×10^{-1}		

[a] 1 cal = 4.184 J).

results indicate that the rate-determining step for solvolyses of **1** involves extensive bond breaking during formation of the transition state. Additional supporting evidence is the similar kinetic solvent isotope effects (KSIE) in methanol (1.22 for **2**[26] and 1.11 for **1**; see footnote to Table 1), although many solvolyses give similar low values for KSIE.[29]

The GW plots [Eqn. (1)] of the rate constants in Tables 1 and 2, presented in Fig. 2 using the solvent ionizing power scale Y_{Cl}, based on 1-adamantyl chloride,[6] show significant dispersion for the aqueous acetone mixtures, with relatively large slopes for alcohol–water ($m = 0.75$, correlation coefficient $r > 0.998$) and acetone–water ($m = 0.90$, $r > 0.999$). Also, the data points for TFE–water and TFE–ethanol show no major deviations from the other correlations.

Table 5. Selectivities (*S*) for solvolyses of cinnamyl chloride in aqueous binary mixtures at 25 °C

	Methanol–water		Ethanol–water	
% (v/v)	[Ether]/[alcohol]	*S*	[Ether]/[alcohol]	*S*
90	12.8	3.20	3.41	1.23
80	6.65	3.73	1.82	1.47
75	5.22	3.90	1.43	1.54
70	4.38	4.21	1.23	1.71
65	3.64	4.40	1.05	1.84
60	3.28	4.91	0.950	2.05
55	2.71	4.99	0.824	2.18
50	2.80	5.36	0.729	2.36
45	2.01	5.51	0.648	2.56
40	1.66	5.61	0.361	2.77

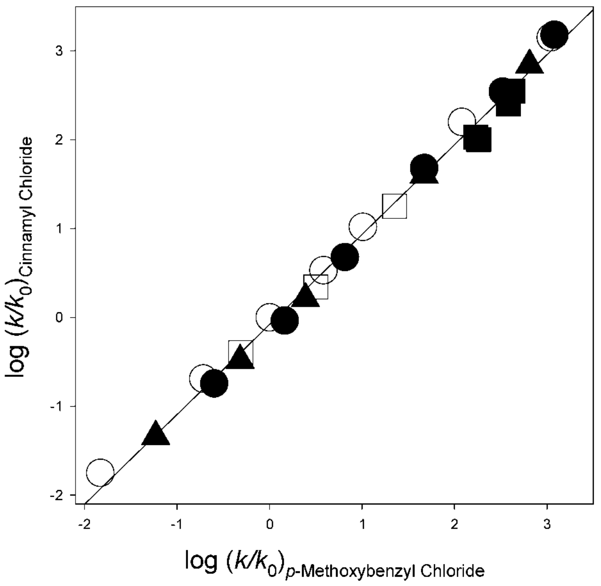


Figure 1. Logarithms of rate constants for solvolyses of cinnamyl chloride vs solvolyses of *p*-methoxybenzyl chloride at 25 °C. Slope = 1.01, *r* = 0.997. Solvents: ●, methanol; ○, ethanol; ▲, acetone; ■, TFE–H_2O; □, TFE–EtOH

Rate ratios in two solvents having the same Y_{Cl} value, i.e. the same degree of solvent assistance for bond cleavage, but different nucleophilicities, provide measures of the minimum extent of nucleophilic solvent assistance,[6,30] and a small value is observed for

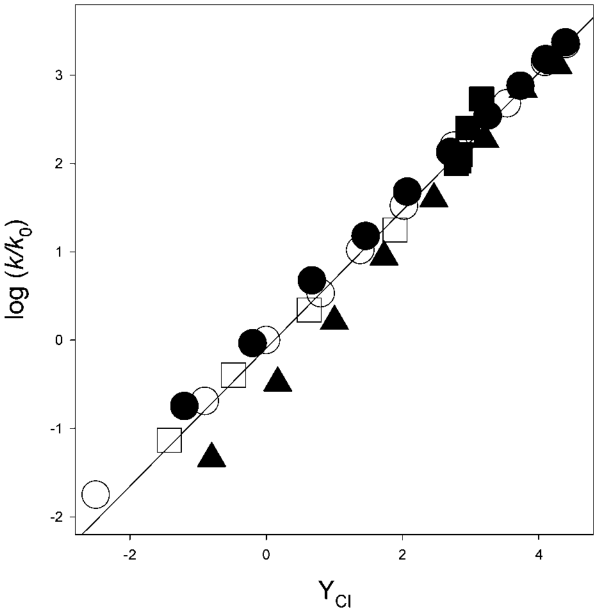


Figure 2. Logarithms of first-order rate constants for solvolyses of cinnamyl chloride at 25 °C: log (k/k_0) vs Y_{Cl}. Solvents: ●, methanol; ○, ethanol; ▲, acetone; ■, TFE–H_2O; □, TFE–EtOH

Table 6. Correlation analyses against different Y, N, I and Y_{sim}

Parameter	n	r	m (SD)[a]	l (SD)[a]	h (SD)[a]
Y_{Cl}	37	0.988	0.76 (0.014)		
Y_{Cl}, N_{OTs}	35	0.988	0.79 (0.022)	0.06 (0.056)	
Y_{Cl}, N_T	24	0.988	0.80 (0.033)	0.06 (0.059)	
Y_{Cl}, I	23	0.988	0.81 (0.031)		0.27 (0.16)
Y_{Cl}, N_{OTs}, I	22	0.992	0.87 (0.028)	0.34 (0.071)	0.88 (0.19)
Y_{Cl}, N_T, I	23	0.992	0.88 (0.041)	0.23 (0.073)	0.56 (0.19)
Y_{sim}[b]	25	0.997	1.01 (0.014)		

[a] Standard deviation.
[b] Log (k/k_0) for p-methoxybenzyl chloride; data from Refs 26 and 28.

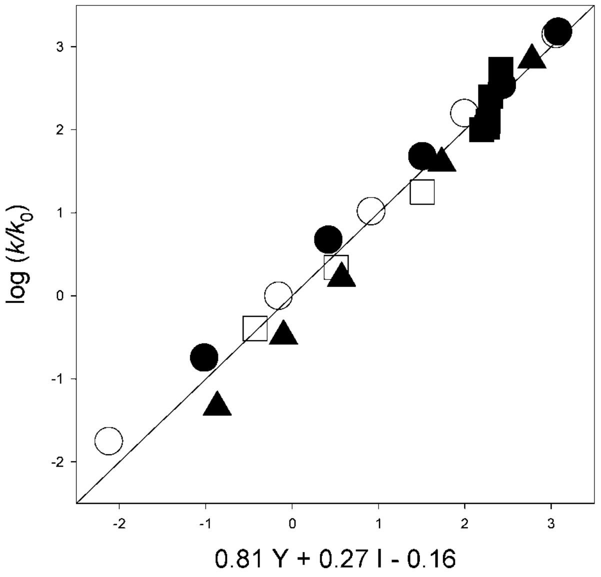


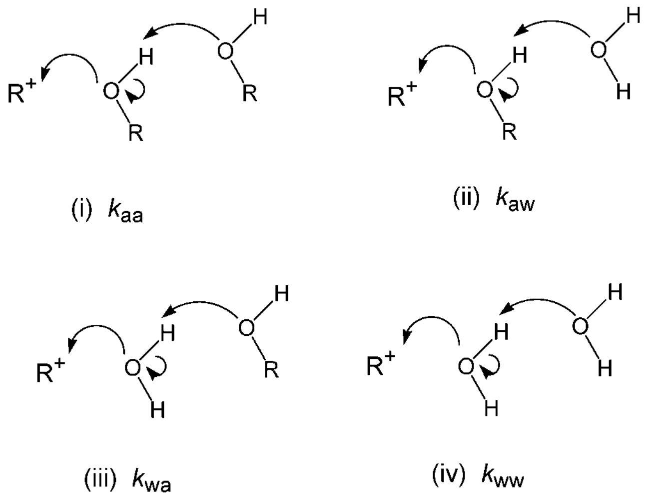
Figure 3. Plot of log(k/k_0) for cinnamyl chloride against $0.81Y + 0.27I - 0.16$; $r = 0.988$. Solvents: ●, methanol; ○, ethanol; ▲, acetone; ■, TFE–H_2O; □, TFE–EtOH

solvolyses of **1** (e.g. $[k_{40EW}/k_{97TFE}]_Y = 1.48$, EW = ethanol–water, Table 2, footnote b). Also, the extended GW Eqn. (2) gives a negligible value for l (Table 6). The results imply that solvolyses of **1** in the binary mixtures proceed by an S_N1 pathway channel with little or no nucleophilic solvent assistance.

Inclusion of the ring parameter (I) gives only a minor improvement to correlations of the solvolyses of **1** using Eqn. (3); although the data for acetone–water again show dispersion (see Fig. 3), the effect is slightly smaller than for Eqn. (1) (see Fig. 2). Dispersions in GW correlations depends on the number of electrons adjacent to the reaction site, with a smaller effect for ethylene and acetylene derivatives than for aromatic systems,[12,16] and the low sensitivity to I ($h = 0.27 \pm 0.16$) is similar to the value of 0.35 for solvolyses of α,γ-dimethylallyl chloride.[16] As Eqn. (4) contains four freely adjustable parameters, the results should be interpreted cautiously;[28] $m = 0.88 \pm 0.04$ [similar to the value obtained using Eqn. (1)] and $c = -0.09$ (small, as expected), but l is ca 0.30 and h is ca 0.6 [it has previously been found that l values obtained using Eqn. (4) are more positive than those calculated using Eqn. (2)].[16]

The product-determining step

The S values are similar to, but slightly lower, than those observed for solvolyses of p-methoxybenzyl chloride (**2**).[24] Constant S values would be expected for competing second-order reactions,[31] and S is very close to constant for solvolyses of 1-adamantyl substrates and for S_N1 reactions of acid chlorides, solvolysing via solvent-separated ion pairs (SSIP).[10,31] During the formation of an SSIP, the nucleophile (alcohol or water) must insert between two ions, and ethanol is less effective than water or methanol (i.e. $S < 1$), whereas $S > 1$ for solvolyses in methanol–water.[10] For solvolyses of **1**, S values for methanol–water mixtures are greater than those for ethanol–water, as observed in general.[31–34] The constant S values for product formation from an SSIP may be explained by nucleophilic attack by the solvent with general base-catalysed assistance by the counteranion.[35]



(i) k_{aa} (ii) k_{aw} (iii) k_{wa} (iv) k_{ww}

Scheme 1. General base-catalysed reactions for nucleophilic attack on carbocations

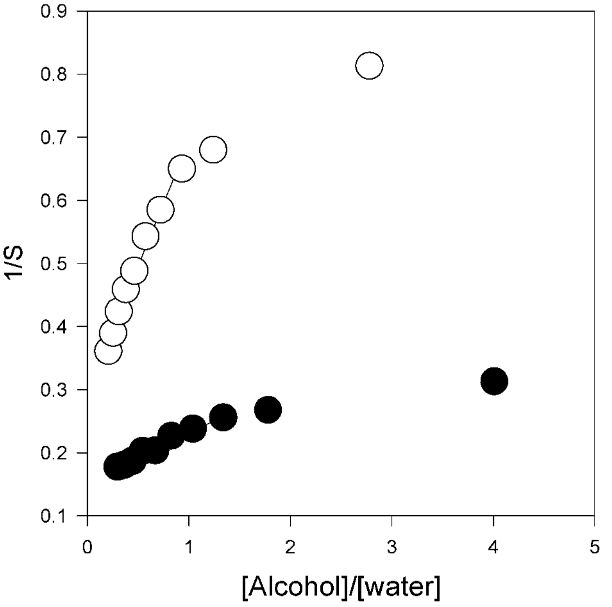


Figure 4. Plot of $1/S$ vs molar ratio of solvents, [alcohol]/[water], for solvolyses of cinnamyl chloride at 25 °C. Solvents: ●, methanol; ○, ethanol, S values from Table 5. For ethanol–water, slope = 0.395, intercept = 0.298, r = 0.982. For methanol–water, slope = 0.078, intercept = 0.153, r = 0.996

However, values of S are rarely constant over a range of compositions of binary aqueous mixtures; usually S values increase as water is added to alcohol (as for solvolyses of **1**, Table 5), so an explanation is required. We propose that the product-determining step is third order, and nucleophilic attack by one solvent molecule is assisted by a second molecule of solvent acting as general base; in alcohol–water mixtures there will then be four competing product-determining steps (Scheme 1) defined by the following third-order rate constants: k_{ww}, where water is both nucleophile and general base; k_{aw}, where the alcohol solvent acts as nucleophile and water acts as general base; k_{wa}, where water acts as nucleophile and alcohol acts as general base; and k_{aa}, where alcohol acts as both nucleophile and general base.[24]

Scheme 1 is of the same kinetic form as the one we have previously derived for acyl[33,34] and sulfonyl[34,36] transfer reactions, which are shown to proceed by S_N2 or addition–elimination reaction mechanisms.[33,34] However, we have reported that the new relationship between S and solvent composition also applied to S_N1 reactions involving nucleophilic attack on carbocations assisted by general base catalysis.[24] It should be noted that in an S_N2 process the rate-determining and product-determining steps are the same, whereas in an S_N1 process the rate depends on the ionizing power of the solvent but the product is determined by the attack of solvent on the cationic intermediate, R^+, i.e. the rate-determining and product-determining steps are not the same.

We assume that the rates of the product-determining reactions shown in Scheme 1 are given by third-order rate constants multiplied by the appropriate bulk molar concentrations of solvent, so we do not allow for any solvent clustering or microenvironments. In a recent search we found no evidence for changes in solvent composition (solvent clustering) at the reaction site, as solvolyses of *p*-methoxybenzoyl chloride (i.e. a neutral substrate, reacting via a very short-lived cationic intermediate) gave almost constant selectivities throughout wide ranges of alcohol–water mixtures.[10,37] In contrast, there is mass spectrometric evidence for tropylium cations solvated by clusters of acetonitrile and alcohols,[38] but these results are not directly comparable to ours.

In highly aqueous media, $k_{aw}[\text{water}][\text{ROH}] \gg k_{aa}[\text{ROH}]^2$, the relationship given in Eqn. (6) can readily be derived.[34] The intercept of Eqn. (6) implies that the maximum S value in highly aqueous media is determined by the ratio of third-order rate constants k_{aw}/k_{ww}; this ratio represents the rate constant for nucleophilic attack by alcohol compared with the rate constant for nucleophilic attack by water, in water as solvent and with water acting as a general base catalyst.

Plots of $1/S$ versus the alcohol/water molar ratio [Eqn. (6)] are linear from 10% to at least 70% alcohol–water mixtures and thereafter curvature is significant (Fig. 4), which is consistent with increasing contributions from the k_{aa} term (Scheme 1).

The selectivities for methanol–water are significantly greater than those for ethanol–water, and the slopes of $1/S$ plots are lower for methanol–water than for ethanol–water (Fig. 4). These trends can be explained by the k_{aw} term, which, compared with the k_{wa} term, is greater for methanol–water than for ethanol–water. The intercept of Eqn. (6) is determined by the ratio of third-order rate constants k_{ww}/k_{aw}, so nucleophilic attack by methanol assisted by water is 6.5 times more favourable than nucleophilic attack by water assisted by water.

Unlike solvolyses of *p*-methoxybenzyl chloride (**2**), which shows common ion rate depression for solvolyses in 50% TFE–water[39] and ethanol–water,[40] there is no common ion depression for solvolyses of cinnamyl chloride (Table 3). Therefore, the product-determining steps must differ. Product formation via a 'free' carbocation is consistent with solvolyses showing a common ion rate depression (e.g. for solvolyses of *p*-methoxybenzyl chloride, **2**). Nucleophilic attack on an SSIP gives a constant selectivity with $S < 1$ for ethanol–water mixtures (see above), so the results for solvolyses of **1** [Eqn. (6) is obeyed, but the common ion effect is absent] require another explanation, probably nucleophilic attack on a contact ion pair.

It has been suggested previously that solvolyses of 1-(4-methylphenyl)ethyl chloride in TFE–water[41] and 1-phenylethyl chloride in methanol[42] react through nucleophilic attack on contact ion pairs. Differences in product-determining steps may be explained by the lifetimes of carbocations, which have been investigated by laser flash photolyses.[43] First-order rates of reaction of the following cations with hexafluoro-2-propanol at 20 °C are as follows: *p*-methoxybenzyl 3×10^2 s^{-1}, 1-(4-methylphenyl)ethyl 5×10^4 s^{-1} and 1-phenylethyl 6×10^5 s^{-1}.[43] Rate constants are much greater in more nucleophilic media,[43] but the order of reactivity is not expected to change;[30] the greater lifetime (smaller rate constant) for the *p*-methoxybenzyl cation is consistent with reaction via nucleophilic attack on a free cation, whereas the other two phenylethyl cations are shorter lived and react via contact ion pairs. Although no data are available for the lifetimes of cinnamyl cations, it is reasonable to suppose that the cinnamyl cation ($\mathbf{1}^+$) is more like a phenethyl cation (and not so stabilized as the *p*-methoxybenzyl cation), and so $\mathbf{1}^+$ reacts via a contact ion pair.

CONCLUSIONS

Solvolyses of cinnamyl chloride (**1**) respond almost identically with those of *p*-methoxybenzyl chloride (**2**) to changes in solvent ionizing power and solvent nucleophilicity (Fig. 1), and products of solvolyses in ethanol– and methanol–water mixtures both obey Eqn. (6). Rates of solvolyses of *p*-methoxybenzoyl chloride also respond to solvent changes very similarly,[26] but the product selectivities are constant for a wide range of ethanol–and methanol–water mixtures.[10] Consequently, although these three substrates solvolyse by very similar rate-determining steps, it appears that each substrate has a different product-determining step; solvolyses of **1** are explained by product formation by general base-catalysed nucleophilic attack on a contact ion pair.

EXPERIMENTAL

Materials. Methanol, ethanol and acetone were of Merck GR grade (<0.1% H_2O) and CH_3OD (99.9% D) was obtained from Aldrich. Distilled water was redistilled with a Buchi Fontavapor 210 and treated using an ELGA UHQ PS to obtain a specific conductivity of less than 1×10^{-6} mho cm^{-1}. Cinnamyl chloride (Aldrich GR grade, 99%) was used without further purification.

Rate measurements and product selectivities. Rate constants were measured conductometrically at 25 (±0.03) °C at least in duplicate, as described previously,[15,26,44] with concentrations of substrate ca 10^{-3} M. The solvolysis products, ether and alcohol, were determined by HPLC analysis as described previously[34,45] and the product selectivities, *S*, were calculated with Eqn. (5). The *S* values were calculated from the observed peak area ratios of ether and alcohol, divided by the appropriate response factor. For response calibrations, area ratios from solvolyses of **1** in pure alcohol and in 40% acetonitrile–water mixtures were used. The eluent was 78% methanol–water and the flow-rate was adjusted to 1 ml min^{-1}. The HPLC system was a Hewlett-Packard 1050 Series instrument with a 250 × 4 mm i.d. Spherisorb ODS reversed-phase column.

Acknowledgements

This research was supported by grant No. KOSEF 2001-1-12300-008-2 from the Korea Science and Engineering Foundation. We are also grateful to D. N. Kevill for helpful discussions.

REFERENCES

1. Winstein S, Grunwald E. *J. Am. Chem. Soc.* 1948; **70**: 846–854.
2. Fainberg AH, Winstein S. *J. Am. Chem. Soc.* 1957; **79**: 1957–1608.
3. Fainberg AH, Winstein S. *J. Am. Chem. Soc.* 1957; **79**: 1608–1612.
4. Winstein S, Fainberg A, Grunwald E. *J. Am. Chem. Soc.* 1957; **79**: 4146–4155.
5. Winstein S, Grunwald E, Jones HW. *J. Am. Chem. Soc.* 1951; **73**: 2700–2707.
6. Bentley TW, Llewellyn G. *Prog. Phys. Org. Chem.* 1990; **17**: 121–158.
7. Bentley TW. In *Nucleophilicity*, Harris JM, McManus SP (eds). *Advances in Chemistry*, vol. 215. 1986; 255–268.
8. Kevill DN. In *Advances in Quantitative Structure–Property Relationships*, vol. 1, Charton M (ed). Jai Press: Greenwich, CT, 1996; 81–115.
9. Bunton CA, Mhala MA, Moffatt JR. *J. Org. Chem.* 1984; **49**: 3639–3641.
10. Bentley TW, Harris HC, Koo IS. *J. Chem. Soc., Perkin Trans. 2* 1988; 783–789.
11. Liu K-T, Sheu HC, Chen H-I, Chiu PF, Hu CR. *Tetrahedron Lett.* 1990; **31**: 3611–3615.
12. Bentley TW, Dau-Schmidt JP, Llewellyn G, Mayr H. *J. Org. Chem.* 1992; **57**: 2387–2392.
13. Bentley TW, Harris HC. *J. Org. Chem.* 1988; **53**: 724–728.
14. Bentley TW, Koo IS. *J. Chem. Soc., Perkin Trans. 2* 1989; 1385–1392.
15. Koo IS, Bentley TW, Kang DH, Lee I. *J. Chem. Soc., Perkin Trans. 2* 1991; 175–9.
16. Kevill DN, Ismail NHJ, D'Souza MJ. *J. Org. Chem.* 1994; **59**: 6303–6312.
17. Kevill DN, D'Souza MJ. *J. Chem. Soc., Perkin Trans. 2* 1995; 973–980.
18. Kevill DN, D'Souza MJ. *J. Chem. Soc., Perkin Trans. 2* 1997; 257–263.
19. Kevill DN, Bond MW, D'Souza MJ. *J. Org. Chem.* 1997; **62**: 7869–7871.
20. Harris JM, Clark DC, Becker A, Fagan JF. *J. Am. Chem. Soc.* 1974; **96**: 4478–4484.
21. Harris JM, Becker A, Fagan JF, Walden FA. *J. Am. Chem. Soc.* 1974; **96**: 4484–4489.
22. Karton Y, Pross A. *J. Chem. Soc., Perkin Trans. 2* 1977; 1860–1863.
23. McLennan DJ, Martin PL. *J. Chem. Soc., Perkin Trans. 2* 1982; 1099–1105.
24. Bentley TW, Ryu ZH. *J. Chem. Soc., Perkin Trans. 2* 1994; 761–767;
25. Ritchie CD. *J. Am. Chem. Soc.* 1971; **93**: 7324–7325.
26. Bentley TW, Koo IS, Norman S. *J. Org. Chem.* 1991; **56**: 1604–1609.
27. Liu K-T, Chen H-I. *J. Chem. Soc., Perkin Trans. 2* 2000; 893–898.
28. Liu K-T, Duann YF, Hou SH. *J. Chem. Soc., Perkin Trans. 2* 1998; 2181–2185.
29. Robertson RE. *Prog. Phys. Org. Chem.* 1963; **4**: 213–280.

30. Bentley TW, Llewllyn G, Ryu ZH. *J. Org. Chem.* 1998; **63**: 4654–4659.
31. Ta-Shma R, Rapport Z. *Adv. Phys. Org. Chem.* 1992; **27**: 239.
32. Koo IS, Yang K, Kang K, Lee I, Bentley TW. *J. Chem. Soc., Perkin Trans. 2* 1998; 1179–1183.
33. Bentley TW, Jones RO. *J. Chem. Soc., Perkin Trans. 2* 1993; 2351–2357.
34. Bentley TW, Jones RO, Koo IS. *J. Chem. Soc., Perkin Trans. 2* 1994; 753–759.
35. Song BD, Jencks WP. *J. Am. Chem. Soc.* 1989; **111**: 8470–8479.
36. Jones RO. M. Phil Thesis. University of Wales. 1991.
37. Bentley TW, Ebdon DN. *Atualidades de Fisico-Quimica Organica*. Florianopolis-SC, Brazil, 1999; 1–14.
38. Kinoshita T, Wakisaka A, Yasumoto C, Takeuchi K, Yoshizawa K, Suzuki A, Yamabe T. *J. Chem. Soc., Chem. Commun.* 2001; 1768–1769.
39. Amyes TL, Richard JP. *J. Am. Chem. Soc.* 1990; **112**: 9507–9512.
40. Queen A. *Can. J. Chem.* 1979; **57**: 2646–2656.
41. Richard JP, Jencks WP. *J. Am. Chem. Soc.* 1984; **106**: 1373–1383.
42. Lee I, Lee WH, Lee HW, Bentley TW. *J. Chem. Soc. Perkin Trans 2* 1993; 141–146.
43. McClelland RA. *Tetrahedron* 1996; **52**: 6823–6858.
44. Koo IS, Yang K, Kang DH, Park HJ, Kang K, Lee I. *Bull. Korean Chem. Soc.* 1999; **20**: 577–580.
45. Yang K, Koo IS, Lee I, Jo D-S. *Bull. Korean Chem. Soc.* 1994; **15**: 280–284.