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Correlation of the Rates of Solvolysis of 1- and 2-Naphthyl Chloroformates Using the Extended Grunwald-Winstein Equation

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The specific rates of solvolysis of 1- naphthyl chloroformate (1-NaphOCOCl, **1**) and 2-naphthyl chloroformate (2-NaphOCOCl, **2**) have been determined in a wide range of solvents at 2.0 and 10.0 °C. These give a satisfactory correlation over the full range of solvents when the extended (two-term) Grunwald-Winstein equation is applied. The sensitivities (*l* and *m*-values) to changes in solvent nucleophilicity (N_T) and solvent ionizing power (Y_{Cl}) are similar to those reported previously for solvolysis of phenyl chloroformate, which has been suggested to proceed through an addition-elimination mechanism with the addition step being rate determining. For four representative solvents, studies were made at several temperatures and activation parameters determined. These observations were also compared with those previously reported for phenyl chloroformates and naphthoyl chlorides.

Key Words : Naphthyl chloroformates, Grunwald-Winstein equation, Addition-Elimination, Solvolysis

Introduction

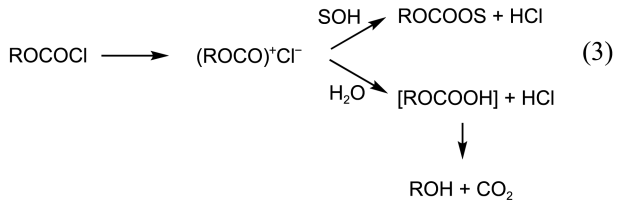
In correlation analyses of the specific rates of solvolysis of alkyl and aryl haloformate esters in a wide range of solvents, we previously obtained very good correlations with the application of the equation (1)[1] and the recognition of two pathways, believed to involve ionization and addition-elimination.

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

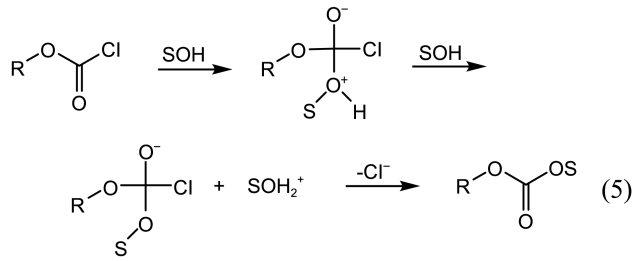
In eqn. (1), k and k_o represent the specific rates of solvolysis in a given solvent and in the standard solvent (80% ethanol), respectively; m is the sensitivity to changes in solvent ionizing power (Y_{Cl});[2] l is the sensitivity to changes in solvent nucleophilicity (N_T)[3] based on the specific rates of solvolysis of the *S*-methyldibenzothiophenium ion, and c is a constant (residual) term. The magnitudes of the l and m values can give important indications regarding the mechanism of solvolysis. In reactions where the reaction site is adjacent to a π-system or in α-haloalkyl aryl compounds that proceed *via* anchimeric assistance, Kevill and co-workers[4] proposed the addition of an aromatic ring parameter (hI) term to equation (1) to give equation (2). h represents the sensitivity to changes in the aromatic ring parameter (I).

$$\log (k / k_o) = lN_T + mY_{Cl} + hI + c \quad (2)$$

Nucleophilic substitution reactions of alkyl chloroformates (ROCOCl) are commonly classified into two types,[5] namely the unimolecular pathway (ionization mechanism, I), involving carboxylium ion intermediate [eqn. (3)] and/or loss of carbon dioxide to give the relatively stable alkyl cation [eqn. (4)], and the bimolecular pathway (addition-elimination mechanism, A-E), which may proceed *via* a tetrahedral intermediate [eqn. (5)].



Scheme 1. Unimolecular Pathway [Ionization Mechanism].



Scheme 2. Bimolecular Pathway [Addition-Elimination Mechanism].

Chloroformate esters with primary alkyl groups are solvolyzed in most of the commonly studies solvents by an addition-elimination mechanism [eqn. (5)] with the addition step being rate-determining. Only in solvents of very low nucleophilicity and very high ionizing power is an ionization mechanism [eqn. (3)] observed.[5(a),(g)] The solvolyses of secondary alkyl chloroformate (*i*-propyl chloroformate)[5(b)] have two major reaction pathways: an addition-elimination pathway [eqn. (5)] involving substitution at acyl carbon in

the more nucleophilic solvents and an ionization pathway [eqn. (4)] involving the loss of carbon dioxide accompanying the substitution in the more ionizing solvents. The tertiary alkyl chloroformate[5(c),(e)] reacts almost exclusively through an ionization pathway [eqn. (4)] which also includes loss of carbon dioxide to give the relatively stable 1-adamantyl cation. We have reported that the solvolyses of phenyl chloroformate (PhOCOCl, **3**)[5(i),(k)] in a wide range of hydroxylic solvents follow an addition-elimination mechanism [eqn. (5)] using the extended Grunwald-Winstein equation (1). And the solvolyses of the naphthoyl chlorides (1-naphthoyl, **6** and 2-naphthoyl chloride, **7**)[6] all favored the ionization pathway except in solvents of high nucleophilicity and low ionizing power.

Alkyl haloformate esters are important reagents which are widely used in physiological and biological studies.[7] Accordingly, the reaction mechanism for solvolysis of alkyl haloformates is a subject of continuing interest in research on this category of compounds. In the present study, we report on the specific rates for solvolyses of **1** and **2** in a variety of pure and binary solvents. The results are also discussed in terms of *l*, *m*, and *h*. In addition to a detailed extended Grunwald-Winstein equation treatment of the specific rates, enthalpies and entropies of activation together with solvent deuterium isotope effect using methanol-*d* have been studied.

Results and Discussion

The specific rates of solvolysis of **1** at 2.0 °C and of **2** at 10.0 °C were measured in a variety of solvents, and presented in Table 1, together with N_T[3], Y_{Cl}[2] and I[4] values. Determination was also made in methanol-*d* (MeOD). For methanol, ethanol, 80% EtOH, and 70% TFE, specific rates of solvolysis of **1** and **2** were measured at three different temperatures, and these values, together with calculated enthalpies and entropies of activation, are summarized in Tables 2 and 3.

In Table 1, the specific rates for the solvolyses of **1** and **2** increase with increasing the water content in all the mixed solvents, indicating that the specific rate is accelerated by the solvent with higher ionizing power (Y_{Cl}). In contrast, solvolyses of **1** and **2** proceed more rapidly with increasing the ethanol content in four binary solvents of TFE-EtOH. These phenomena are similar to those studied previously for **3** in various solvents,[5(i),(k)] which have been suggested to proceed through an addition-elimination mechanism with the addition step being rate determining.

For solvolyses in ethanol, methanol, 80% ethanol, and 70% TFE, the values of the enthalpy and the entropy of activation for the solvolysis of **1** and **2** (Tables 2 and 3) are 11.1~14.4 kcal mol^{-1} and −32.7 ~ −24.4 cal mol^{-1} K^{-1}, respectively. In Tables 2 and 3, the large negative entropies of activation observed for **1** and **2** in four solvents are consistent with the bimolecular nature of the rate-determining step. The mechanism for solvolyses of **1** and **2** is similar to that reported for solvolyses of methyl chloroformate[5(a)] and ethyl chloroformate[5(g)] in four or five solvents, which have been suggested to proceed through a bimolecular channal.

Table 1. Specific rates of solvolysis of 1-naphthyl chloroformate (**1**)[a] at 2.0 °C and 2-naphthyl chloroformate (**2**)[b] at 10.0 °C in a variety of pure and mixed solvents

Solvent[c]	$10^4 k_{1\text{-Nap}}$ (s^{-1})[d]	$10^4 k_{2\text{-Nap}}$ (s^{-1})[d]	N_T[e]	Y_{Cl}[f]	I[g]
100% MeOH	18.9 ± 0.3[h]	30.1 ± 0.1[i]	0.17	-1.17	0.41
90% MeOH	30.1 ± 0.2	57.1 ± 0.3	-0.01	-0.18	-
80% MeOH	37.7 ± 0.1	86.2 ± 0.2	-0.06	0.67	0.14
70% MeOH	43.6 ± 0.1	-	-0.40	1.46	0.05
100% EtOH	5.89 ± 0.05	8.60 ± 0.04	0.37	-2.52	0.20
90% EtOH	9.62 ± 0.11	17.3 ± 0.1	0.16	-0.94	-
80% EtOH	10.7 ± 0.1	21.1 ± 0.3	0.00	0.00	0.00
70% EtOH	10.9 ± 0.1	24.0 ± 0.01	-0.20	0.78	-
60% EtOH	11.5 ± 0.5	27.6 ± 0.4	-0.38	1.38	-0.15
50% EtOH	11.7 ± 0.1	33.6 ± 0.1	-0.58	2.02	-0.20
90% Acetone	1.01 ± 0.01	1.37 ± 0.01	-0.35	-2.39	-0.17
80% Acetone	1.85 ± 0.02	3.13 ± 0.01	-0.37	-0.80	-0.23
70% Acetone	2.74 ± 0.06	5.08 ± 0.01	-0.42	0.17	-0.29
60% Acetone	3.71 ± 0.01	7.57 ± 0.04	-0.52	1.00	-0.28
40% Acetone	6.49 ± 0.05	15.8 ± 0.04	-0.83	2.46	-0.35
70% TFE	0.241 ± 0.012	0.564 ± 0.024	-1.98	2.96	0.25
50% TFE	0.659 ± 0.019	1.73 ± 0.02	-1.73	3.16	0.09
60T-40E[j]	0.424 ± 0.001	0.72 5± 0.001	-0.94	0.63	0.59
40T-60E[j]	1.53 ± 0.01	2.44 ± 0.02	-0.34	-0.48	0.43
20T-80E[j]	3.50 ± 0.01	5.41 ± 0.02	0.08	-1.42	0.31

[a]Substrate concentration of 3.00~4.00 × 10^{-3} mol dm^{-3}. [b]Substrate concentration of 1.00~3.00 × 10^{-4} mol dm^{-3}. [c] Volume/volume basis at 25.0 °C, except for TFE-H_2O mixtures, which are on a weight/weight basis. [d]The average of all integrated specific rates from duplicate runs, with associated standard deviation. [e]From ref. 3. [f]From ref. 2. [g]From ref. 4. [h]Value in MeOD of (7.60 ± 0.17) × 10^{-4} s^{-1}, and solvent deuterium isotope effect (k_{MeOH}/k_{MeOD}) of 2.49 ± 0.02. [i]Value in MeOD of (12.4 ± 0.2) × 10^{-4} s^{-1}, and solvent deuterium isotope effect (k_{MeOH}/k_{MeOD}) of 2.43 ± 0.02. [j]T-E are 2,2,2-trifluoroethanol-ethanol mixtures.

The solvent deuterium isotope effect (k_{MeOH}/k_{MeOD}) (footnote to Table 1) for methanolysis is 2.49 at 2.0 °C for **1** and 2.43 for **2** at 10.0 °C. These values are of a magnitude usually taken to indicate that nucleophilic attack by a methanol molecule is assisted by general-base catalysis by a second methanol molecule (Scheme 2).[8] The solvent deuterium isotope effect has previously been studied for several solvolyses of haloformate esters. In methanol, the k_{MeOH}/k_{MeOD} ratio was in the range of 2.14 to 2.22 for the solvolyses of primary alkyl chloroformates (methyl chloroformate, ethyl chloroformate and *n*-propyl chloroformate) which have been reported to proceed through a bimolecular mechanism.[5] The k_{MeOH}/k_{MeOD} values for *i*-propyl chloroformate[9] and *t*-butyl fluoroformate[10] in the ionization range, were somewhat lower at 1.25 in pure water and 1.26 in methanol, respectively.

A useful test in considering detailed mechanisms of solvolysis is to carry out a correlation analysis using the extended Grunwald-Winstein equation [eqn. (1)] and compare the *l* and *m* values with those reported previously for

Table 2. Specific rates of solvolysis of **1** at various temperatures and enthalpies ($\Delta H^{\neq}$, kcal mol^{-1}) and entropies ($\Delta S^{\neq}$, cal mol^{-1} K^{-1}) of activation

Solvent[a]	Temp. (°C)	$10^4\,k$ (s^{-1})[b]	$\Delta H^{\neq}_{275}$[c]	$\Delta S^{\neq}_{275}$[c]
100% MeOH	2.0	18.9 ± 0.3[d]	11.5±0.8	-28.9±2.8
	5.0	24.6 ± 0.2		
	10.0	33.3 ± 0.8		
	15.0	52.7 ± 1.7		
100% EtOH	2.0	5.89 ± 0.05[d]	11.1±0.2	-32.7±0.7
	5.0	10. 3± 0.3		
	10.0	14.9 ± 0.1		
	15.0	22.0 ± 0.4		
80% EtOH	2.0	10.7 ± 0.1[d]	11.3±0.3	-31.1±1.1
	5.0	13.1 ± 0.1		
	10.0	19.2 ± 0.1		
	15.0	28.3 ± 0.2		
70% TFE	40.0	6.66 ± 0.36	14.1±0.2	-28.3±0.6
	50.0	13.2 ± 0.8		
	55.0	18.7 ± 0.8		
	60.0	24.6 ± 0.3		

[a,b]See footnotes Table 1. [c]With associated standard error. [d]From Table 1.

Table 3. Specific rates of solvolysis of **2** at various temperatures and enthalpies ($\Delta H^{\neq}$, kcal mol^{-1}) and entropies ($\Delta S^{\neq}$, cal mol^{-1} K^{-1}) of activation

Solvent[a]	Temp. (°C)	$10^4\,k$ (s^{-1})[b]	$\Delta H^{\neq}_{283}$[c]	$\Delta S^{\neq}_{283}$[c]
100% MeOH	5.0	20.3 ± 0.3	11.2±0.3	-30.5±1.0
	10.0	30.1 ± 0.1[d]		
	15.0	41.7 ± 1.2		
	20.0	60.9 ± 0.3		
100% EtOH	10.0	8.60 ± 0.04[d]	11.8±0.2	-30.9±0.7
	15.0	12.4 ± 0.2		
	20.0	18.1 ± 0.1		
	25.0	25.7 ± 0.1		
80% EtOH	5.0	13.7 ± 0.4	13.1±0.2	-24.4±0.8
	10.0	21.1 ± 0.3[d]		
	15.0	33.0 ± 0.2		
	20.0	48.2 ± 0.1		
70% TFE	10.0	0.564 ± 0.024[d]	14.4±0.1	-27.1±0.3
	40.0	7.06 ± 0.11		
	45.0	10.4 ± 0.1		
	50.0	15.2 ± 0.1		

[a,b]See footnotes Table 1. [c]With associated standard error. [d]From Table 1.

other haloformate esters. The correlations using the specific rates for **1** and **2** of the pure and binary solvents reported in Table 1 within the simple Grunwald-Winstein equation [eqn. (1) without the lN$_T$ term] result in an extremely poor correlation coefficient (R). For the solvolyses of **1** and **2**, the analyses in terms of the extended Grunwald-Winstein equation [eqn. (1)] of the data for the specific rates lead to a satisfactory linear correlation with values of 1.59 ± 0.15 and 1.60 ± 0.14 for l, 0.40 ± 0.05 and 0.45 ± 0.05 for m, 0.18 ± 0.07 and 0.14 ± 0.07 for c, and 0.934 and 0.942 for the correlation coefficient, respectively. The plots of correlations

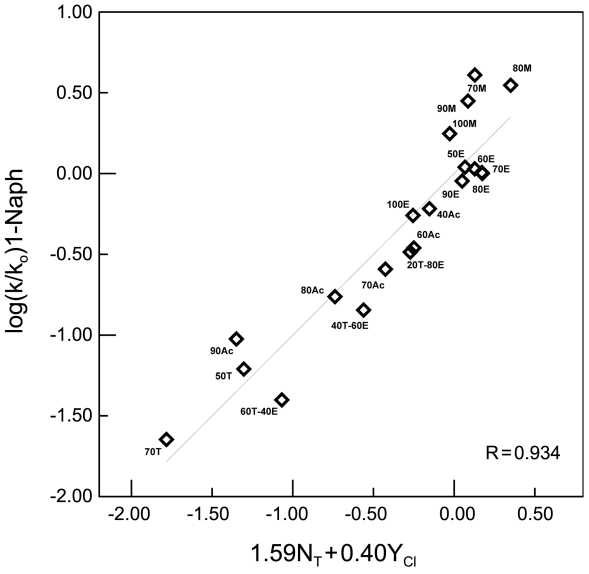


Figure 1. Plot of log (k/k_o) for solvolyses of 1-naphthyl chloroformate (**1**) against (1.59N_T + 0.40Y_{Cl}) in various binary solvents at 2.0 °C.

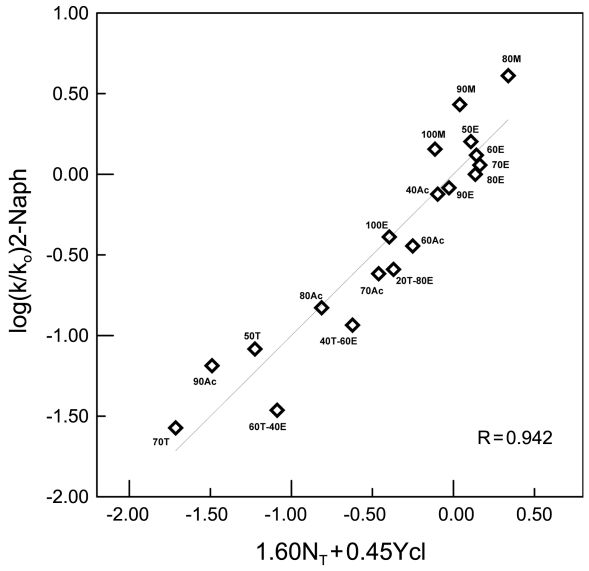


Figure 2. Plot of log (k/k_o) for solvolyses of 2-naphthyl chloroformate (**2**) against (1.60N_T + 0.45Y_{Cl}) in various binary solvents at 10.0 °C.

of the specific rates of solvolysis of **1** and **2** are shown in Figures 1 and 2.

The results of the correlation analysis in terms of equations (1) and (2) are shown in Table 4, together with the corresponding parameters obtained in the analyses of earlier studied substrates. The l/m ratio has been suggested as a useful mechanistic criterion and the values in Table 4 divide nicely into two classes with values of 2.80 to 3.67 for those entries postulated to represent addition-elimination pathway (Scheme 2) and 0.27 to 0.61 for those believed to represent ionization pathway (Scheme 1). The l/m ratios of 3.56 and 3.98 obtained for **1** and **2** are similar to those reported previously for reactions suggested to proceed through a

Table 4. Correlation of the specific rates of solvolysis of **1** and **2**, and a comparison with the corresponding specific rate values for aromatic chloroformate esters (**3**, **4**, **5**, **6**, and **7**) using various forms of the Grunwald-Winstein equation

Substrate	Mech.[a]	n^b	l^c	m^c	h^c	$c^{c,d}$	l/m	R[e]
1[f]		20		-0.05 ± 0.09		-0.33 ± 0.15		0.122
	A-E	20	1.59 ± 0.15	0.40 ± 0.05		0.18 ± 0.07	3.98	0.934
		17	1.57 ± 0.17	0.40 ± 0.06	-0.06 ± 0.23	0.16 ± 0.09		0.938
2[f]		19		-0.02 ± 0.09		-0.40 ± 0.15		0.057
	A-E	19	1.60 ± 0.14	0.45 ± 0.05		0.14 ± 0.07	3.56	0.942
		17	1.54 ± 0.16	0.43 ± 0.06	-0.15 ± 0.21	0.11 ± 0.08		0.948
3[g]	A-E	44	1.60 ± 0.05	0.54 ± 0.03		0.15 ± 0.06	2.96	0.979
		44	1.67 ± 0.08	0.57 ± 0.04	0.19 ± 0.20	0.15 ± 0.06		0.979
4[h]	A-E	38	1.69 ± 0.07	0.46 ± 0.04		0.07 ± 0.08	3.67	0.974
5[g]	A-E	44	1.60 ± 0.05	0.57 ± 0.05		0.18 ± 0.06	2.80	0.981
		44	1.70 ± 0.08	0.61 ± 0.04	0.29 ± 0.18	0.19 ± 0.06		0.982
6[i]	I	20	0.17 ± 0.11	0.62 ± 0.07		0.12 ± 0.09	0.27	0.925
		20	0.28 ± 0.10	0.67 ± 0.06	0.77 ± 0.25	0.11 ± 0.08		0.953
7[i]	I	32	0.31 ± 0.07	0.51 ± 0.04		0.11 ± 0.08	0.61	0.921
		31	0.39 ± 0.09	0.54 ± 0.05	0.33 ± 0.24	0.12 ± 0.08		0.923

[a]Addition-elimination (A-E) and ionization (I). [b]Number of solvent systems included in the correlation. [c]Using G-W equation with standard errors for *l*, *m*, and *h* values and with the standard errors of the estimate accompanying the c values. [d]Constant (residual) term. [e]Correlation coefficient. [f]This work. [g]Values taken from ref. 5 (i). [h]Values taken from ref. 5(j). [i]Values taken from ref. 6(a).

bimolecular pathway such as solvolysis of *p*-nitrophenyl chloroformate (**4**),[5(j)] and methyl chlorothioformate (l/m = 3.4),[11(a)] neophenthyl chloroformate (l/m=3.7)[11(b)] and phenyl chlorothioformate (l/m=3.6)[11(c)] in all the solvents except high ionizing and low nucleophilic solvents.

Unlike the solvolyses of **6**, where significant sensitivity (h) towards changes in the I parameter was observed, the solvolyses of **1** and **2** together with **3**, *p*-methoxyphenyl chloroformate (**5**) and **7** led to negligible h values (Table 4). Kevill *et al.* and other authors[6] have proposed previously that the development of positive charge at the reaction center (carbonyl carbon), and steric hindrance to the approach to the carbonyl carbon from the *peri*-hydrogen on C-8 of 1-naphthyl chloride (**6**) lead to an increased sensitivity toward changes in the solvation effects at the aromatic rings. Substrates **1** and **2** lead to correlation with unexpected negative sensitivity (h) to changes in the aromatic ring parameter (I). Recently, Martins and co-workers[12(a)] have suggested that the negative h values often arise since I is not a pure parameter but it includes a solvent nucleophilicity component. Accordingly, in the present study, the negative sensitivity (h) to changes in the I parameter gives insignificant meaning, namely it means that the π-charge delocalization effect is not developed at the reaction center due to an adjacent oxygen atom on naphthyl group in solvolysis of **1**.[6,12]

To prove further the similarity between solvent effects upon the specific rates of solvolysis of **1**, **2** and **4**, we have constructed plots of log $(k/k_o)_4$ for *p*-nitrophenyl chloroformate (**4**) against log $(k/k_o)_1$ for 1-naphthyl chloroformate (**1**) or against log $(k/k_o)_2$ for 2-naphthyl chloroformate (**2**) in Figure 3. The plots show a good linearity (correlation coefficients, R=0.982 and 0.975). Since solvolysis of *p*-nitrophenyl chloroformate (**4**)[5(j)] is believed to proceed through

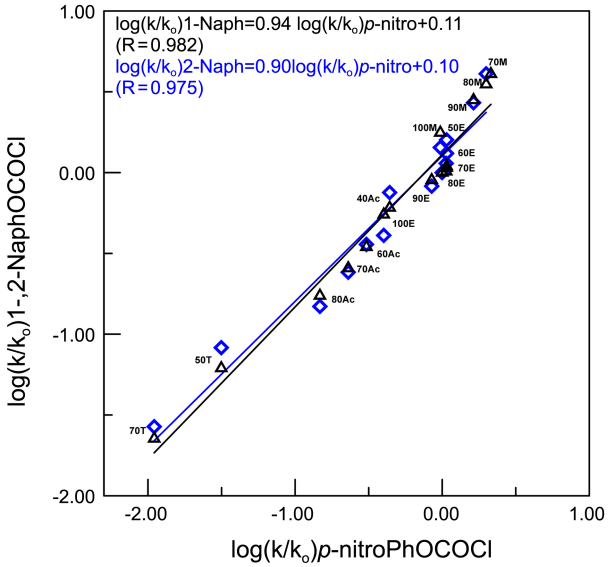


Figure 3. Plots of log (k/k_o) for solvolyses of 1- and 2-naphthyl chloroformates (**1** and **2**) against log (k/k_o) for solvolyses of *p*-nitrophenyl chloroformate (**4**).

an addition-elimination pathway in all the solvents involved in the plots, the similarity in l and m-values for the two solvolyses (**1** and **2** against **4**) gives rather strong evidence for an addition-elimination mechanism.

Conclusions

The solvolyses of **1** and **2** involving an addition-elimination mechanism (A-E), with the addition step being rate determining (eqn. 5), are supported by three types of evidence obtained in this study. Firstly, the l and m values (l/m values) obtained for the solvolyses of **1** and **2** using an extended

Grunwald-Winstein equation (eqn. 1) are similar to those for other chloroformate esters, which have been reported to proceed through an addition-elimination pathway (A-E) with addition step being rate determining. Secondly, the solvent deuterium isotope effect value for methanolysis (k_{MeOH}/k_{MeOD}) is of a magnitude usually taken to indicate that nucleophilic attack by a methanol molecule is assisted by general-base catalysis by a second methanol molecule. Thirdly, the large negative entropies of activation observed for the solvolyses of **1** and **2** in four solvents are consistent with the bimolecular nature of the rate-determining step. In the present study, unlike the solvolyses of naphthoyl chlorides (**6** and **7**), where an ionization pathway was reported, the solvolyses of **1** and **2** proceed through an addition-elimination pathway with the addition step being rate determining.

Experimental

Naphthyl chloroformate (**1**, Aldrich) and 2-naphthyl chloroformate (**2**, Aldrich) were used without further purification. Solvents were purified and the kinetic runs carried out as previously described.[10]

The kinetic measurements were made conductometrically using a Metrohm 712 (Swiss), with an immersion measuring cell (Pt 100). All runs were performed in duplicate with at least 150 readings taken at appropriate intervals over three half-lives and infinity readings taken after ten half-lives. The rates of production of hydrochloric acid were followed for solvolyses in ethanol and methanol and in binary mixtures of water with ethanol (EtOH), methanol (MeOH), acetone, and 2,2,2-trifluoroethanol (TFE), and also in binary mixtures of 2,2,2-trifluoroethanol and ethanol (T-E). The *l* and *m* values were calculated using commercially available computer programs for multiple regression analyses.

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