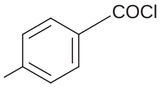
Stoichiometric solvation effects. Part 3. Product–rate correlations for solvolyses of *p*-nitrophenyl chloroformate in alcohol–water mixtures

In Sun Koo,*[,a] Kiyull Yang,[a] Keumduck Kang,[a] Ikchoon Lee[b] and T. William Bentley[c]

[a] *Department of Chemical Education, Gyeongsang National University, Chinju, 660-701, Korea*
[b] *Department of Chemistry, Inha University, Incheon, 402-751, Korea*
[c] *Department of Chemistry, University of Wales, Swansea, UK SA2 8PP*

Rate constants for solvolyses of *p*-nitrophenyl chloroformate in water, D_2O, CH_3OD, 50% D_2O–CH_3OD, and in aqueous binary mixtures of acetone, acetonitrile, ethanol and methanol are reported at 25 °C. Product selectivities are reported at 25 °C for a wide range of ethanol–water and methanol–water solvent compositions. Plots of first-order rate constants *vs.* Y_{Cl} (based on rates of solvolyses of 1-adamantyl chloride) give three separate curves for the aqueous mixtures with a small m value and unusual rate maxima for aqueous alcohol solvents. To account for these results, third-order rate constants k_{ww} and k_{aa} were calculated from the rate constants observed in pure solvents, together with k_{aw} and k_{wa} calculated from the intercept and slope of the plot of S *vs.* [water]/[alcohol] or *via* computer fitting. The calculated rate constants, k_{calc} and mol% of ester agree satisfactorily with the experimental values, supporting the stoichiometric solvation effect analysis. The kinetic solvent isotope effects determined in water and methanol are consistent with the proposed mechanism—a general base catalysed addition-elimination.

Rate constants for solvolyses of neutral substrates (RX) usually increase when water is added to alcohols (such as ethanol or methanol), as expected for reactions in which charge is developed in the transition state and the solvent polarity is increased.[1] Plots of rates of solvolyses in binary aqueous mixtures against solvent composition or solvent polarity very rarely show rate maxima; two published examples are solvolyses of methyl perchlorate in acetone– and dioxane–water[2] and of *p*-nitrobenzoyl chloride **1** ($Z = NO_2$) in aqueous alcohols.[3] Very recent results for solvolyses of *p*-methoxyphenyl chloroformate **2** ($Z = OMe$)[4] and for ethyl chloroformate[5] show rate maxima in aqueous methanol, but not in aqueous ethanol. We now report kinetic data for a third chloroformate example, solvolyses of *p*-nitrophenyl chloroformate **2** ($Z = NO_2$), which shows marked rate maxima in both aqueous ethanol and aqueous methanol.



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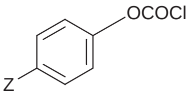

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The products of competing nucleophilic substitution reactions in alcohol–water mixtures can be interpreted in terms of product selectivities, S, defined from molar ratios of products and of solvents [eqn. (1)]. If these reactions simply involved

$$S = [\text{ester product}][\text{water}]/[\text{hydrolysis product}][\text{alcohol}] \quad (1)$$

competitive attack upon the substrate by either water or alcohol, S values would be independent of solvent composition, as is observed for solvolyses occurring *via* solvent separated ion pair intermediates.[6] More typically S values often increase in more aqueous media when reactivity usually increases; this trend is difficult to explain[7] and is contrary to that expected from the reactivity-selectivity principles (RSP).[8]

We have shown recently, for a wide range of solvolyses, that the increase in solvolysis rates and the increase in S can be related to solvent stoichiometry [eqns. (2) and (3)], if it is

$$1/S = (\text{slope})([\text{alcohol}]/[\text{water}]) + (\text{intercept}) \quad (2)$$

$$S = (\text{slope})([\text{water}]/[\text{alcohol}]) + (\text{intercept}) \quad (3)$$

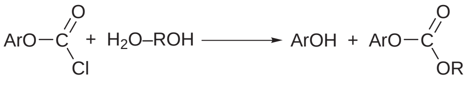
assumed that the product forming steps are second order in solvent.[3,9] For solvolyses of **1** ($Z = NO_2$)[3] and **2** ($Z = OMe$),[4] a second order dependence on solvent (third order overall) can also explain the unusual rate maxima noted above. We now report a third example.

Third order processes can be established directly from the observed rate law for solvolyses of **1** ($Z = NO_2$) in acetonitrile containing small amounts of methanol.[10] It is thought that one molecule of solvent acts as a nucleophile and a second molecule acts as a general base.[10] Methanol probably acts as both nucleophile and general base, because large rate enhancements are observed when chloride ion (a base in acetonitrile) is added, while only minor rate enhancements are observed when phenol is added.[10] A competing process may be pseudo-second order, and may involve methanol as nucleophile with acetonitrile, present in large excess, acting as general base.[10]

Depending on reaction conditions, substrates and solvent compositions, nucleophilic reactions of acyl halides were reported as addition-elimination (S_AN), S_N1 or S_N2 reaction mechanisms.[11] Based on product–rate studies, benzoyl chloride **1** ($Z = H$) solvolyses by an S_N2 mechanism in high polarity solvents, whereas it favors a general base catalyzed S_AN pathway in less polar media.[12,13] Solvolyses of chloroformates are known to occur predominantly by an S_AN pathway;[14] recent interest centres on correlations of solvolysis rates using the extended Grunwald–Winstein equation,[15] particularly the separation of observed reaction rates into contributions from competing S_AN and ionisation reaction channels.[5,16]

Results

Solvolyses of aryl chloroformates [eqn. (4)] in alcohol–water mixtures lead to a phenol (ArOH) and an ester (ArOCOOR). Rate constants for solvolyses of *p*-nitrophenyl chloroformate **2** ($Z = NO_2$) in methanol–, ethanol–, acetone–, acetonitrile– and



$$ArO{-}C(=O)Cl + H_2O{-}ROH \longrightarrow ArOH + ArO{-}C(=O)OR \quad (4)$$

Table 1 Rate constants for solvolyses of *p*-nitrophenyl chloroformate **2** ($Z = NO_2$) in aqueous methanol, ethanol, acetone, acetonitrile and dioxane at 25 °C[a]

Alcohol[b] (%, v/v)	$k/10^{-1}$ s^{-1}				
	MeOH	EtOH	Acetone	MeCN	Dioxane
100	1.35	0.557			
90	2.27	1.18			
80	2.77	1.39	0.205	0.0593	0.262
70	2.98	1.48	0.319	0.0938	0.425
60	2.94	1.49	0.425	0.135	0.589
50	2.75	1.49	0.517	0.189	0.751
40	2.39	1.42	0.611	0.275	0.831
30	1.91	1.28	0.687	0.400	0.851
20	1.48	1.09	0.696	0.559	0.794
10	1.08	0.892	0.727	0.696	0.564
H_2O	0.776	0.776	0.776	0.776	0.776

[a] Determined conductimetrically at least in duplicate; average deviation <3%. [b] 10 ml water is added to 90 ml methanol to make a 90% v/v methanol–water mixture.

Table 2 Selectivities for solvolyses of *p*-nitrophenyl chloroformate **2** ($Z = NO_2$) in alcohol–water mixtures at 25 °C[a,b]

Alcohol[c] (%, v/v)	Methanol–water		Ethanol–water	
	[ester]/[acid]	*S*	[ester]/[acid]	*S*
97	40.4	2.81	13.9	1.39
95	26.4	3.12	9.14	1.56
93	19.2	3.26	7.09	1.73
90	12.4	3.63	5.50	1.98
87	11.9	3.98	4.91	2.38
83	9.24	4.27	3.92	2.60
80	8.42	4.73	3.17	2.57
70	5.80	5.56	2.49	3.46
60	4.35	6.52	1.95	4.21
50	3.28	7.38	1.48	4.79
40	2.44	8.24	1.07	5.20
30	1.68	8.82	0.69	5.21
20	1.01	9.09	0.38	4.86
10	0.49	9.89	0.16	4.67

[a] Determined by duplicate HPLC analyses of each solvent composition; average deviation <1%. [b] Injected 5 μl of a 10% solution of **2** ($Z = NO_2$) in acetonitrile into 5 ml of solvent. [c] See footnote *b*, Table 1.

Table 3 Kinetic solvent isotope effects (KSIE) for solvolyses of *p*-nitrophenyl chloroformate **2** ($Z = NO_2$) at 25 °C

Solvent	k_{SOH}	k_{SOD}	KSIE
Methanol	1.35×10^{-1}	6.43×10^{-2}	2.10
50% Methanol	2.75×10^{-1}	1.34×10^{-1}	2.05
Water	7.66×10^{-2}	4.38×10^{-2}	1.75

dioxane–water mixtures at 25.0 °C are summarised in Table 1. Product selectivities [*S*, eqn. (1)] are given in Table 2, and kinetic solvent isotope effects are shown in Table 3.

Discussion

Rate constants (Table 1) increase in the order acetonitrile–H_2O < acetone–H_2O < dioxane–H_2O < EtOH–H_2O < MeOH–H_2O, and show maxima near 70% methanol–water (70M) in aqueous methanol mixtures and near 60% ethanol–water (60E) in aqueous ethanol mixtures. The rate increases only two- to three-fold as the water content of the mixtures increases; this means that the rate is slightly accelerated by the solvent with higher ionizing power, *Y*, suggesting that bond breaking in the transition state is of little importance. Similarly, first-order rate constants for solvolysis of **1** ($Z = NO_2$) vary over only a three-fold range in alcohol–water mixtures.

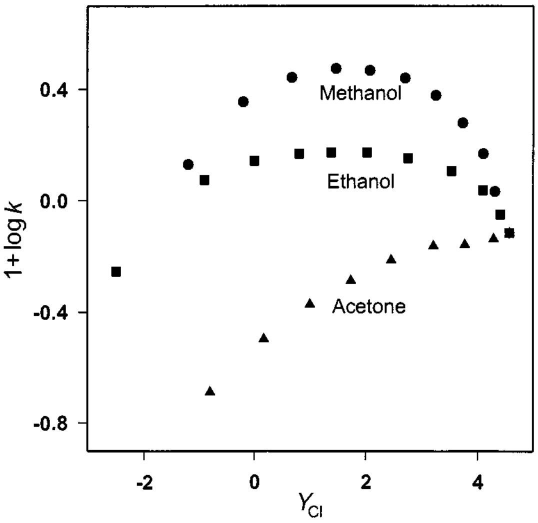


Fig. 1 Logarithms of first-order rate constants for solvolyses of *p*-nitrophenyl chloroformate **2** ($Z = NO_2$) at 25 °C *vs.* Y_{Cl} (ref. 17)

Grunwald–Winstein plots (Fig. 1) using the Y_{Cl} scale of solvent ionizing power, based on solvolyses of 1-adamantyl chloride [eqn. (5)],[17] show that three of the aqueous mixtures

$$\log(k/k_o)_{RX} = mY_{Cl} \qquad (5)$$

exhibit dispersions into separate curves. The plot for acetone–water shows a very small *m* value, *m* = 0.12 (*r* = 0.995), implying that the solvolysis of **2** ($Z = NO_2$) in the binary mixture proceeds by the addition-elimination (S_AN) or associative S_N2 reaction channels rather than by an S_N1 mechanism.

Product selectivities (*S*, Table 2) reveal that for aqueous methanol mixtures the selectivity increases with increasing water content, whereas the selectivity exhibits a maximum in aqueous ethanol; thus the reactivity-selectivity principle (RSP)[8] is not obeyed in methanol and partially obeyed (up to 30% ethanol–water) in ethanol mixtures. The greater value of *S* in more aqueous media for **2** ($Z = NO_2$) is a strong indication that the role of alcohol as a nucleophile is important while the effect of ionizing power is insignificant in the product determining step of the reaction of **2** ($Z = NO_2$). Similar selectivity changes have been shown to be typical for a general base-catalysed carbonyl addition-elimination channel in aqueous alcohol media.[3,9]

The occurrence of general base catalysis is supported by the kinetic solvent isotope effects (KSIE), k_{SOH}/k_{SOD}, using deuterated water (D_2O) and methanol (CH_3OD). Previous work indicated that the KSIE value is relatively large (1.7) for a general base-catalysed reaction, but it is small (1.2–1.5) for S_N2 reactions.[18] For solvolyses of **2** ($Z = NO_2$), the KSIE is larger than 1.7 in methanol, 50% aqueous methanol and water; the KSIE is the same for methanol and 50% aqueous methanol (Table 3).

Eqns. (2) and (3) account for the solvent dependence of product selectivities in alcohol–water mixtures;[3,19] these two equations are successful for the product-forming steps of reactions of free cations,[20] and for concerted nucleophilic substitution reactions.[3]

The Grunwald–Winstein plot (Fig. 1) in unusual because it shows a low response to solvent ionizing power, and maxima in reactivity at 70% methanol–water (70M) and 60% ethanol–water (60E). Both rates and products can be explained by stoichiometric solvation effects based on a third-order reaction mechanism. Interpretations based on a third-order mechanism are more complex in alcohol–water mixtures than in pure solvents, but significant new information is available because two products are formed. For solvolyses in binary mixtures, there are four possible third order rate constants: (i) k_{aa} for a mechanism in which one molecule of alcohol acts as a nucleophile and second molecule acts as a general base; (ii) k_{aw} in which alcohol

Table 4 Third-order rate constants, k_{ww}, k_{aw}, k_{wa} and k_{aa} for solvolyses of *p*-nitrophenyl chloroformate **2** (Z = NO_2) in alcohol–water mixtures

		$k/10^{-5}$ M^{-2} s^{-1}			
Plot	Solvent	k_{ww}	k_{aw}	k_{wa}	k_{aa}
1/*S*[a]	Methanol	2.49	24.9	1.94	22.1
S[b]	Methanol	2.49	37.0	8.67	22.1
Computer[c]	Methanol	2.49	44.1	8.59	22.1
1/*S*[a]	Ethanol	2.49	16.5	3.17	18.9
S[b]	Ethanol	2.49	35.5	15.9	18.9
Computer[c]	Ethanol	2.49	44.0	16.4	18.9

[a] 1/*S* plot: eqns. (2) and (8), Fig. 2. [b] *S* plot: eqns. (3) and (10), Fig. 3. [c] Computer fitting (using the program SIGMA PLOT) of data for 80–97% methanol–water and 83–97% ethanol–water to show the similarity with results from *S* plots.

acts as a nucleophile and water acts as a general base; (iii) k_{wa} in which water acts as nucleophile and alcohol acts as general base; and (iv) k_{ww} in which water acts as both nucleophile and general base.[3,9] Therefore, observed first-order rate constants in alcohol–water mixtures are given by eqn. (6).

$$k_{obs} = k_{aa}[\text{alcohol}]^2 + (k_{aw} + k_{wa})[\text{alcohol}][\text{water}] + k_{ww}[\text{water}]^2 \quad (6)$$

The k_{aa} terms can be calculated from observed first order rate constants in pure alcohol ($k_{aa} = k_{obs}/[ROH]^2$); similarly k_{ww} can be obtained from the observed first order rate constant in water ($k_{ww} = k_{obs}/[H_2O]^2$).[3,9] In order to determine k_{aw} and k_{wa} terms, it is necessary to have product selectivity data as well as kinetic data. Assuming that the contribution of k_{aa} to the observed reaction is neglected (*e.g.* for mixtures of low alcohol content), *S* [eqn. (1)] is then given by eqn. (7), and the reciprocal simplifies to eqn. (8).[3,9] The derivation of eqn. (8) implies that it may

$$S = \{(k_{aw}[\text{alcohol}][\text{water}])/(k_{wa}[\text{alcohol}][\text{water}] + k_{ww}[\text{water}]^2)\} \times [\text{water}]/[\text{alcohol}] \quad (7)$$

$$1/S = (k_{wa}/k_{aw})([\text{alcohol}]/[\text{water}]) + k_{ww}/k_{aw} \quad (8)$$

be possible to calculate the observed first-order rate constants if one of the three third-order rate constants is known. We calculated k_{ww} as described above, and then k_{aw} and k_{wa} were obtained from the intercept and slope of Fig. 2, respectively. The third-order rate constants are summarised in Table 4.

Independent measures of k_{wa} and k_{aw} can be obtained from the product ratios in 83–97% alcohol–water and the observed rate constant in pure alcohol, because if the k_{ww} term is ignored, *S* is given by eqn. (9) which can be simplified to eqn. (10).[3]

$$S = \{(k_{aa}[\text{alcohol}]^2 + k_{aw}[\text{alcohol}][\text{water}])/k_{wa}[\text{alcohol}][\text{water}]\} \times ([\text{water}]/[\text{alcohol}]) \quad (9)$$

$$S = (k_{aw}/k_{wa})([\text{water}]/[\text{alcohol}]) + k_{aa}/k_{wa} \quad (10)$$

Experimental tests of eqn. (10) shown in Fig. 3 show a good correlation with the molar ratio of solvent to at least 83% alcohol–water mixtures. Slopes and intercepts of eqn. (10) provide independent measures of the absolute values of k_{aw} and k_{wa} (Table 4). Values of k_{aw} derived from the *S* plot [eqn. (10)] for both methanol–water and ethanol–water mixtures agree satisfactorily (within a factor of two) with those derived independently from the 1/*S* plot [eqn. (8)]. However, values of the smaller k_{wa} rate constant vary over a wider range (four- to five-fold), in part because the assumption on which eqn. (8) is based is not valid over the whole range of solvents shown in Fig. 2.[3] A computer fit, without approximations due to neglected terms, gives very similar results to those based on the *S* eqn. (10)—see Table 4.

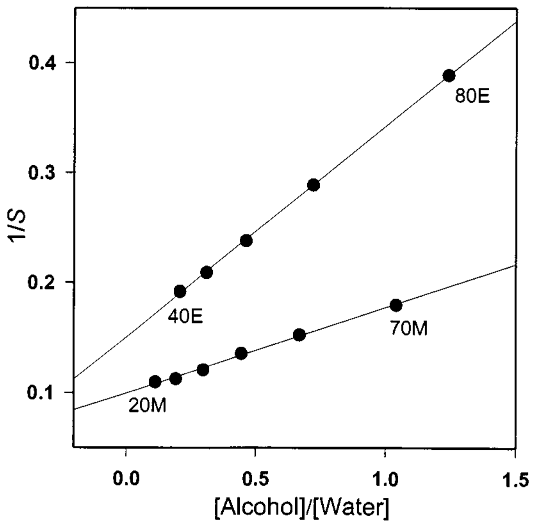


Fig. 2 Correlation of 1/*S* and alcohol–water molar ratio for solvolyses of *p*-nitrophenyl chloroformate **2** (Z = NO_2). For methanol–water: slope = 0.0779, intercept = 0.0998, *r* = 0.996. For ethanol–water: slope = 0.192, intercept = 0.151, *r* = 1.00.

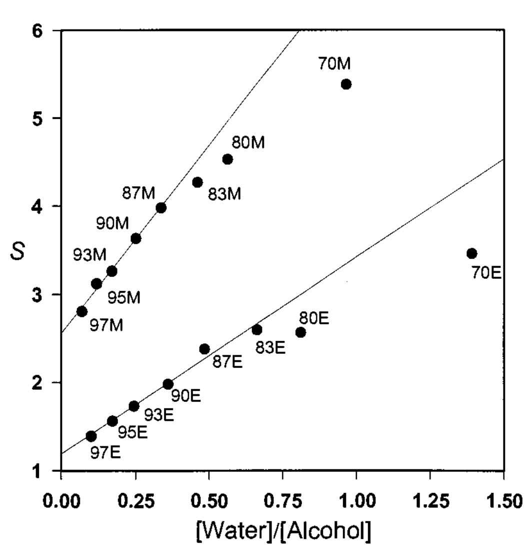


Fig. 3 Correlation of *S* and alcohol–water molar ratio for solvolyses of *p*-nitrophenyl chloroformate **2** (Z = NO_2). For methanol–water: slope = 4.27, intercept = 2.55, *r* = 0.993. For ethanol–water: slope = 2.23, intercept = 1.19, *r* = 0.984.

The calculated first-order rate constants (k_{calc}), contributions of third-order terms to k_{calc} [using eqn. (11)], observed percentage of ester, and calculated percentage of ester [using eqn. (12)] are summarised in Table 5.

$$k_{calc} = k_{ww}[\text{water}]^2 + (k_{wa} + k_{aw})[\text{water}][\text{alcohol}] + k_{aa}[\text{alcohol}]^2 \quad (11)$$

$$\text{mol\% of ester} = (k_{aw}[\text{water}][\text{alcohol}] + k_{aa}[\text{alcohol}]^2)/k_{calc} \quad (12)$$

The rate constant is predicted to be a maximum in 50E and 60M, in close agreement with the observed result (Table 5). A comparison of observed and calculated first-order rate constants for ethanol–water mixtures, calculated using eqn. (11), is given in Fig. 4; agreement is reasonably good, *e.g.* in 70% ethanol–water (70E), the difference in the first-order rate constant is only 4% and the difference in the mol% ester is only 7%. Such good agreement between calculated and experimental values (Table 5) implies that the use of eqn. (10) in the analysis of stoichiometric solvation effects and reaction mechanism is justified.

Table 5 Calculated rate constants, k_{calc}, and contributions of third-order terms to k_{calc}, with calculated percentage ester product for *p*-nitrophenyl chloroformate **2** ($Z = NO_2$) solvolyses in aqueous methanol (M) and ethanol (E)[a]

Alcohol (%, v/v)	$k/10^{-1}$ s^{-1}		$k/10^{-3}$ s^{-1}				Ester (%)	
	k_{calc}	k_{obs}	k_{aa}	k_{aw}	k_{wa}	k_{ww}	Obs.	Calc.
90M	1.75	2.27	109	54.4	10.6	0.77	93.6	93.5
80M	2.05	2.77	86.3	96.7	18.8	3.07	89.0	89.3
70M	2.19	2.98	60.1	127	24.7	6.90	84.8	85.6
60M	2.34	2.94	48.5	145	28.3	12.3	81.3	82.6
50M	2.33	2.75	33.7	151	29.4	19.2	76.6	79.1
40M	2.13	2.39	21.6	135	28.3	27.6	70.8	73.8
30M	2.01	1.91	12.1	127	24.7	37.6	62.7	69.0
20M	1.70	1.48	5.39	96.7	18.8	49.1	50.2	60.1
10M	1.28	1.08	1.35	54.4	10.6	62.1	31.7	43.1
90E	0.974	1.18	44.9	37.7	14.0	0.767	89.3	84.8
80E	1.31	1.39	35.5	67.0	25.0	3.07	84.4	78.6
70E	1.55	1.48	27.2	87.8	32.7	6.90	80.9	74.5
60E	1.70	1.49	20.0	100	37.4	12.3	76.8	70.7
50E	1.77	1.49	13.9	105	39.0	19.2	71.5	67.1
40E	1.75	1.42	8.87	100	38.1	27.6	64.5	62.5
30E	1.73	1.28	4.99	87.8	32.8	37.6	53.9	59.3
20E	1.43	1.09	2.22	67.0	25.0	49.1	39.9	48.1
10E	1.14	0.89	0.55	37.7	14.0	62.1	21.4	33.2

[a] Values of k_{aw} and k_{wa} were obtained from the computer fit (Table 4).

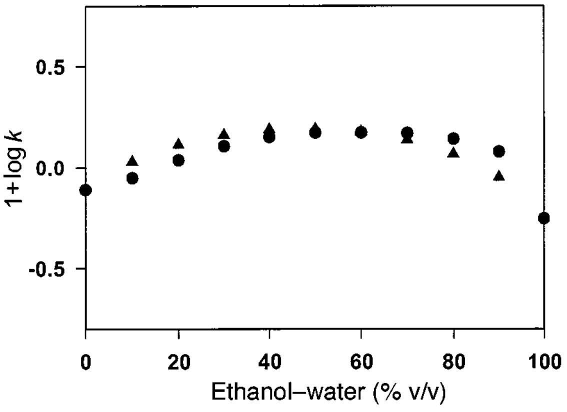


Fig. 4 Comparison of logarithms of (▲) calculated and (●) observed first-order rate constants for solvolyses of *p*-nitrophenyl chloroformate **2** ($Z = NO_2$) in ethanol–water at 25 °C

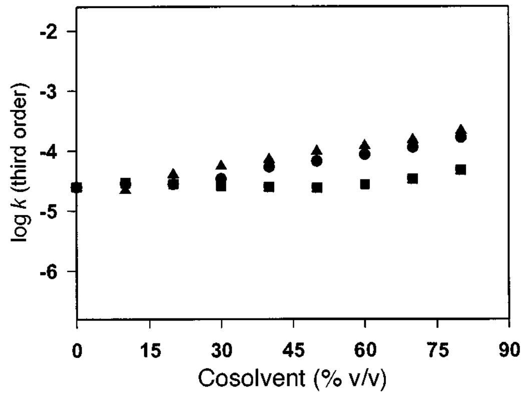


Fig. 5 Plot of logarithms of third-order rate constants for solvolyses of *p*-nitrophenyl chloroformate **2** ($Z = NO_2$) in (●) acetone–, (■) acetonitrile– and (▲) dioxane–water mixtures against percentage cosolvent

According to the third-order treatment, the individual contributions of the four third-order terms to the observed first order rate constants (Table 5) show that k_{aw} (*i.e.* methanol is acting as a nucleophile and water is acting as a general base catalyst) makes the largest contributions in all but one of the solvent compositions (the exception is 90% alcohol–water). The importance of [alcohol][water] terms is at a maximum in 50% alcohol–water mixtures, and so solvent stoichiometry can explain the occurrence of unusual rate maxima for solvolyses in alcohol–water mixtures;[2,3] maxima would be observed when one or both of the two [alcohol][water] terms dominate, and when there is a very small dependence of rate on solvent polarity.

The third-order rate constants, k_{aw} and k_{aa}, in which alcohol acts as a nucleophile are larger than k_{wa} and k_{ww} terms in which water acts as a nucleophile (Table 4). In the (k_{wa} + k_{aw})-[water][alcohol] term of eqn. (6), k_{aw} is greater than k_{wa}, and third-order rate constants (k_{aw}) are very similar for methanol and ethanol. Catalysis of nucleophilic attack by water is favoured by ethanol ($k_{wa} = 16.4 \times 10^{-5}$ dm^6 mol^{-2} s^{-1}, Table 4) > methanol ($k_{wa} = 8.6 \times 10^{-5}$ dm^6 mol^{-2} s^{-1}) > water ($k_{ww} = 2.49 \times 10^{-5}$ dm^6 mol^{-2} s^{-1}); as this is not the accepted order of pK_a values for these weak acids,[21] the second solvent molecule may act not only as a general base but also as a hydrogen-bond donor to the carbonyl oxygen.

For acetone–, acetonitrile– and dioxane–water mixtures, calculated third-order rate constants vary over a three-fold range with changes in solvent composition (Fig. 5), whereas the observed first-order rate constants vary over a 13-fold range (Table 1); the complex patterns of the results (Fig. 5) may be explained by the assumption that the aprotic solvents are acting as weak general bases[10a,22] or nucleophiles,[23] so accounting for the small increase in the third-order rate constant in less aqueous mixtures. Eqn. (13) was found to be successful for

$$k_{obs}/[\text{water}]^2 = k_{ww} + k_{wc}[\text{cosolvent}]/[\text{water}] \qquad (13)$$

correlating such effects for solvolyses of *p*-nitrobenzoyl chloride,[3a] but it is much less satisfactory for solvolyses of *p*-nitrobenzenesulfonyl chloride, especially for dioxane–water mixtures.[9] However, eqn. (13) is found to be successful for correlating such effects for solvolyses of *p*-nitrophenyl chloroformate **2** ($Z = NO_2$), especially for acetone–water and acetonitrile–water mixtures. Plots (Fig. 6) of third-order rate constants against molar ratios of [cosolvent]/[water] for solvolyses of **2** ($Z = NO_2$) in acetone–water (slope = 14.9, intercept = 2.59, $r = 0.986$) and acetonitrile–water (slope = 1.54, intercept = 2.34, $r = 0.806$) mixtures show that the k_{wc} value for the acetone–water solvent mixture is 10 times greater than that for acetonitrile–water solvent mixtures, and it implies that the role of cosolvent as a general base catalyst is more important in acetone than in acetonitrile. General base catalysis by cosolvent

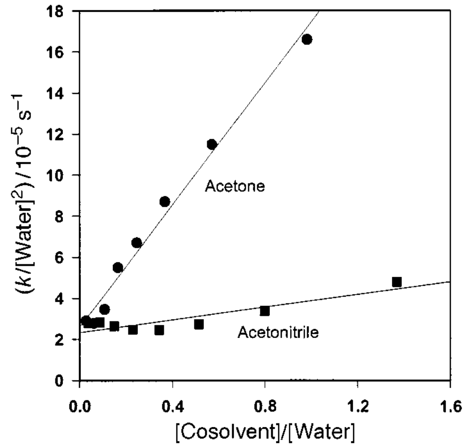


Fig. 6 Plot of third-order rate constants for solvolyses of *p*-nitrophenyl chloroformate **2** ($Z = NO_2$) in acetone–water (slope = 14.9, intercept = 2.59, $r = 0.986$) and acetonitrile–water (slope = 1.54, intercept = 2.34, $r = 0.806$) mixtures against [cosolvent]/[water]

is favoured in the increasing order of hydrogen-bond acceptor basicity of cosolvents [acetone ($\beta = 0.48$) > acetonitrile ($\beta = 0.31$)].[24]

Conclusions

Four competing third-order processes explain the main features of both the rates and the products of solvolyses of *p*-nitrophenyl chloroformate **2** ($Z = NO_2$) in ethanol– and methanol–water mixtures. The most important pathway, involving the alcohol acting as the nucleophile and water acting as a general base, explains the unusual rate maxima (Fig. 1) and the tendency for the product selectivity [*S*, eqn. (1)] to increase as the reactivity increases (contrary to the RSP). Other factors, such as initial state effects,[25] may become significant in highly aqueous mixtures. Our results provide a further example (in addition to previous results for halides,[3,10] esters[26] and amides[27]) of third order acyl transfers in protic media.

Experimental

Materials

Methanol, ethanol and acetone were Merck GR grade (<0.1% H_2O), and D_2O and CH_3OD were from Aldrich (99.9% D). Distilled water was redistilled in a Buchi Fontavapor 210 and treated using ELGA UHQ PS to obtain a specific conductivity of less than 1×10^{-6} S cm^{-1}. *p*-Nitrophenyl chloroformate **2** ($Z = NO_2$) was Aldrich Gr grade (99.8%). The solvents for kinetic studies and for HPLC were as described previously.[12a]

Rate measurements and product selectivities

The rates were measured conductometrically at 25.00 (±0.03) °C, at least in duplicate as described previously,[12] with concentrations of substrate *ca.* 10^{-3} M.

The solvolysis products, ester and *p*-nitrophenol, were determined by HPLC analysis as described previously,[3] and the product-selectivities, *S*, were calculated from eqn. (1). The *S* values were calculated from the observed peak area ratios of ester and *p*-nitrophenol, divided by the appropriate response factor. For response calibrations, area ratios from solvolyses of **2** ($Z = NO_2$) in pure alcohol and in 40% acetonitrile–water mixtures were used. The eluent was a 60% methanol–water mixture and the flow rate was adjusted to 1 ml min^{-1}. The HPLC system was a Hewlett-Packard 1050 Series instrument, with 250 × 4 mm Spherisorb ODS reversed phase column.

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