Correlation of the rates of solvolysis of 3,4,5-trimethoxy- and 2,4,6-trichlorobenzoyl chlorides Kyoung-Ho Park and Dennis N. Kevill*

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The introduction of methoxy groups into the 3- and 5-positions of 4-methoxybenzoyl chloride leads to a reduction in specific rates of solvolysis. An extended Grunwald–Winstein equation correlation for the specific rates of solvolysis of 3,4,5-trimethoxybenzoyl chloride gives sensitivities towards changes in solvent nucleophilicity (/value) of 0.29 and towards changes in solvent ionising power (*m* value) of 0.54. The low *m* value allows specific rates to be determined in highly ionising fluoroalcohol-H₂O mixtures. A parallel correlation of the specific rates of solvolysis of 2,4,6-trichlo-robenzoyl chloride reveals that solvolyses in 100% and 90% ethanol or methanol do not appreciably follow the ionisation pathway indicated for solvolyses in the other solvents and it is proposed that, despite the two *ortho*-substituents, the addition–elimination pathway has become dominant.

Keywords: trisubstituted benzoyl chlorides, linear free energy relationships, Grunwald-Winstein equation, kinetics and mechanism, substituent effects

One aspect of the present report involves a study of the rates of solvolysis of 3,4,5-trimethoxybenzoyl chloride (1). There have been extensive studies of 4-methoxybenzoyl chloride (2) solvolyses.¹⁻⁶ In reactions of 1, the powerful resonance electron donation of the *para*-methoxy group will be moderated not only by its own electron withdrawing inductive effect but also by the inductive effect of the two *meta*-methoxy groups. The 4-methoxybenzoyl chloride has been studied in 40 solvents but for many of these solvents, including the important solvents rich in 1,1,1, 3,3,3-hexafluoro-2-propanol (HFIP), values at 25.0 °C had to be estimated by an Arrhenius-type extrapolation of values obtained at lower temperatures. The retarding influence of the two *meta*-methoxy substituents allows the kinetics of solvolysis of 1 to be studied directly at 25.0 °C over a much wider range of solvents.

We have recently reported⁷ the correlations of the rates of solvolysis of a series of dichlorobenzoyl chlorides, including 2,6-dichlorobenzoyl chloride (**3**) and 2,4-dichlorobenzoyl chloride (**4**). We now report the specific rates of solvolysis of 2,4,6-trichlorobenzoyl chloride (**5**) in a wide variety of hydroxylic solvents. The consequences following from the introduction of a third chlorine into the aromatic ring can be considered either as regards its introduction into the *para*position of **3** or as regards its introduction into the remaining *ortho*-position of **4**.

It has been shown⁸ that the specific rates of solvolysis of benzoyl chloride and its derivatives over a wide range of hydroxylic solvents can be conveniently correlated using an extended form⁹⁻¹² of the Grunwald–Winstein equation (1).¹³ In Eqn (1), *k* and k_0 are the

$$\log (k/k_o)_{\rm RX} = lN_{\rm T} + mY_{\rm x} + c \tag{1}$$

specific rates (first-order rate coefficients) for solvolysis of a substrate RX in a given solvent and in the standard solvent (80% ethanol–20% water v/v), respectively, *m* is the sensitivity to changes in solvent ionising power (Y_X for a leaving-group X), *l* is the sensitivity to changes in solvent nucleophilicity (N_T values based on solvolyses of the *S*-methyldibenzothiophenium ion are usually used), and *c* is a constant (residual) term. Tabulations of Y_x^{14} and N_T^{15} values are available.

The solvolyses of acyl chlorides can be considered in terms of two mechanisms. An ionisation mechanism is shown as Scheme 1. Indications are, however, that this mechanism is frequently subject to an appreciable nucleophilic assistance from the solvent. This can be pictured either in terms of nucleophilic solvation of a developing acylium ion^{7,8} or in terms of a borderline $S_N 1-S_N 2$ pathway.^{1,2} An alternative pathway, involving nucleophilic addition to the carbonyl group is shown in Scheme 2.

Deprotonation of the first formed intermediate in Scheme 2 (general-base catalysis) allows progression to product by an overall addition–elimination (association-dissociation) pathway.^{1,2,8,16} The solvolyses of *p*-nitrobenzoyl chloride (**6**), in all studied solvents except 97% HFIP, are believed to follow this mechanism.⁸

Results and discussion

The first-order rate coefficients (specific rates) for solvolysis were obtained using a rapid response conductivity technique for 31 solvents with **1** at 25 °C and for 28 solvents with **5** at 55.0 °C. These values are reported in Table 1. The solvents used in the study consisted of ethanol, methanol and 2,2,2-trifluoroethanol (TFE) and, for each, a series of mixtures with



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Table 1 First order rate coefficients for solvolyses of 3,4,5-trimethoxybenzoyl chloride (1) at 25.0 °C and 2,4,6-trichlorobenzoyl chloride (5) at 55.0 °C

Solvent ^a	10 ³ k (1)/s ⁻¹	10 ³ k(2)/s ^{-1b}	10 ³ <i>k</i> (5)/s ⁻¹	<i>k</i> (5)/ <i>k</i> (3)
100% EtOH	0.712 ± 0.001	0.936	0.0162 ± 0.0002	1.76
90% EtOH	2.33 ± 0.01	5.55	0.0496 ± 0.0001	1.08
80% EtOH	4.90 ± 0.01	22.4	0.108 ± 0.001	0.72
70% EtOH	9.61 ± 0.03	63.2	0.244 ± 0.002	0.53
60% EtOH	18.9 ± 0.1	181	0.580 ± 0.001	0.42
50% EtOH	41.9 ± 0.2	576 ^d	1.64 ± 0.01	0.39
100% MeOH	4.59 ± 0.01	9.57	0.0846 ± 0.0009	0.84
90% MeOH	10.5 ± 0.1	36.0	0.218 ± 0.001	0.65
80% MeOH	21.9 ± 0.1	124	0.523 ± 0.001	0.50
70% MeOH	43.6 ± 0.2	320	1.28 ± 0.01	0.45
60% MeOH	74.8 ± 0.2	834°	3.05 ± 0.01	0.40
50% MeOH	127.0 ± 1	2400		
90% Acetone	0.154 ± 0.001			
80% Acetone	0.703 ± 0.003	2.67	0.0111± 0.0001	1.27
70% Acetone	7.99 ± 0.04	11.6	0.0441± 0.0003	0.97
60% Acetone	14.5 ± 0.1	50.9	0.185 ± 0.001	0.48
50% Acetone	20.8 ± 0.2	212 ^f		
100% TFE ^g	15.5 ± 0.1	501	0.833 ± 0.011	0.24
97% TFE ^g	16.8 ± 0.1	566 ^h	0.542 ± 0.002	0.25
90% TFE ^g	23.5 ± 0.2		0.745 ± 0.001	0.25
80% TFE ^g	34.7 ± 0.3		1.28 ±0.01	0.22
70% TFE ^g	48.4 ± 0.1	1800 ^{<i>h</i>}	2.16 ± 0.01	0.25
60% TFE ^g	67.6 ± 0.2	3.50 ± 0.03	0.24	
50% TFE ^g	96.6 ± 0.1	6.42 ± 0.21	0.24	
80T-20E	6.22 ± 0.01	110	0.128 ± 0.002	0.27
60T-40E	2.90 ± 0.01	30.2	0.0465 ± 0.0003	0.33
40T-60E	1.55 ± 0.01	8.67	0.0219 ± 0.0002	0.34
20T-80E	0.995 ± 0.003			
97% HFIP ⁹	138 ± 1	27x10 ³	12.7 ± 0.1	0.23
90% HFIP ⁹	84.0 ± 0.2		6.34 ± 0.03	0.26
70% HFIP ⁹	81.3 ± 0.1		6.18 ± 0.02	0.26

^aPrepared on a volume/volume basis at 25.0 °C, unless otherwise stated.

^bUnless otherwise stated, from ref. 5.

^cValues for **3** at 55.0 °C. from ref. 7.

^dRef. 1 gives value of 541.

^eRef. 1 gives value of 844.

^fRef. 1 gives value of 229.

^gSolvent prepared on weight/weight basis.

^{*h*}Values from ref. 2.

ⁱValue from ref. 6 (obtained by Arrhenius extrapolation of values at -20.15 and -9.90 °C).

water. Specific rates of solvolysis were also determined in mixtures of water with HFIP and acetone and in mixtures of ethanol with TFE. Also contained within Table 1 are literature values for the specific rates of solvolysis of **2** at 25.0 °C^{1,2,5,6} and the ratios of the specific rates for **5** relative to **3**⁷ at 55.0 °C.

It was possible for **1** to obtain specific rates of solvolysis at 25.0 °C over the full range of solvents usually included in Grunwald–Winstein correlation studies. Surprisingly, in pure ethanol, the specific rates were only slightly lower than for **2**, despite the addition of the two electron-withdrawing methoxy substituents. As can be seen from the data reported in Table 1 for the solvolyses of **1** and **2**, the differences become greater as the water content increases and, for 50% ethanol, the retardation is by a factor of about 13. Similar trends are observed for aqueous methanol and aqueous acetone. The two *meta*-substituents lead to large retardations in TFE and in TFE–water mixtures. The retardation is by a factor of 32 in 100% TFE, and the value increases only slightly to 34 in 97% TFE (w/w) and to 37 in 70% TFE (w/w).

The behaviour can be examined in terms of a log–log plot of the data for **1** against the data for **2**. Plots of log (k/k_o) for an aroyl chloride against log (k/k_o) for **2** have been shown previously ³ to be a very useful probe for ionisation character in the solvolyses of an aroyl chloride. Figure 1 shows a plot of log (k/k_o) for **1** against log (k/k_o) for **2**.⁸ There is some degree of scatter but no constant trends that could correspond to a solvent-induced change in mechanism, The correlation coefficient for the 22 point plot is reasonably good at 0.931, the slope of the plot is 0.61 ± 0.05 , and the intercept is 0.01 ± 0.06 . The slope is lower than might have been anticipated, showing that the specific rates for solvolyses of **1** are less sensitive towards solvent variation than those for **2**. The correlation values allow a specific rate value of 9713 to be calculated for 97% HFIP. This is only 36% of the recently estimated⁶ value. Indeed, inspection of Fig. 1 shows that all the fluoroalcohol-containing solvents lie below the correlation line.

Another approach to comparing the behaviour of **1** and **2** under solvolytic conditions is to apply the extended Grunwald–Winstein equation to the specific rates of solvolysis of each compound and to compare the sensitivity values (*l* and *m*) obtained. Using the experimental specific rates at 25.0 °C and the tabulated N_T^{15} and Y_{Cl}^{14} values, the *l* and *m* values for **1** can be compared to those previously reported ⁸ for **2** and with new values for **2** incorporating in the analysis three recently reported⁶ specific rates (Table 2). The sensitivities to changes in solvent nucleophilicity are essentially identical and the observed differences in response to solvent variation are due to differences in the sensitivities towards changes in solvent ionising power, with *m* values of 0.54 ± 0.04 for **1** (Fig. 2) very low for an ionisation pathway, and of 0.81 ± 0.02 for **2**, typical for an ionisation pathway.

The hydroxy and methoxy substituents are frequently put forward as examples of substituents where the Hammett



Fig. 1 Plot of $\log(k/k_o)$ for the solvolyses of 3,4,5-trimethoxybenzoyl chloride (1) at 25.0 °C against $\log(k/k_o)$ for 4-methoxybenzoyl chloride (2) at 25.0 °C.

Table 2 Correlation on the specific rates of solvolysis of several derivatives of benzoyl chloride using the extended Grunwald-Winstein equation (1)

Substrate	T °C	nª	ľ	m ^b	C ^b	R°	l/m
3,4,5 (MeO) 1	25.0	31 ^d	0.32 ± 0.05	0.54 ± 0.04	0.09 ± 0.05	0.960	0.59
		27 ^{<i>e</i>,,<i>f</i>}	0.34 ± 0.04	0.59 ± 0.03	-0.02 ± 0.05	0.975	0.58
4 (MeO) 2 ^g	25.0	37 ^{<i>h</i>}	0.31 ± 0.05	0.81 ± 0.02	0.08 ± 0.06	0.989	0.38
		40 ^{<i>i</i>}	0.30 ± 0.04	0.83 ± 0.02	0.04 ± 0.05	0.988	0.36
		37 ^j	0.29 ± 0.03	0.87 ± 0.02	-0.08 ± 0.05	0.993	0.33
2,6 (CI) 3 ^k	55.0	30	0.29 ± 0.07	0.74 ± 0.05	0.10 ± 0.07	0.965	0.39
2,6 (CI) 3 ^k	55.0	26 ^e	0.35 ± 0.06	0.86 ± 0.05	-0.07 ± 0.07	0.975	0.41
2,4 (CI) 4 ^k	55.0	21'	1.46 ± 0.16	0.41 ± 0.05	0.21 ± 0.07	0.911	3.56
2,4 (CI) 4 ^k	55.0	10 ^m	0.32 ± 0.02	0.87 ± 0.03	-2.80 ± 0.07^{n}	0.996	0.37
2,4,6 (CI) 5	55.0	27	0.29 ± 0.08	0.62 ± 0.07	0.05 ± 0.08	0.931	0.46
2,4,6 (CI) 5	55.0	23 ^e	0.40 ± 0.06	0.82 ± 0.06	-0.21 ± 0.08	0.967	0.49
4 (NO ₂) 6 ^g	25.0	34	1.78 ± 0.08	0.54 ± 0.04	$0.11 \pm 0.37^{\circ}$	0.969	3.30

^aNumber of solvents

^bWith associated standard error.

^cMultiple correlation coefficient.

^dF-test value of 159.

^ePoints for 100% ethanol, 100% methanol, 90% ethanol and 90% methanol removed from the

correlation.

^fF-test value of 231 ^gFrom ref. 8.

^hF-test value of 630.

⁷From refs. 6 and 8 (values for 97% HFIP, acetic and formic acids from ref.6); F-Test value of 772.

¹As immediately above entry, but with 100% EtOH, 100% MeOH and 90% EtOH removed; *F*-test value of 1229. ^kFrom ref. 7

In EtOH-H₂O, MeOH-H₂O, acetone-H₂O, and TFE-EtOH.

^mIn TFE-H₂O and HFIP-H₂O.

ⁿLarge negative value because the k_o value is for the bimolecular pathway.

^oAccompanied by the standard error of the estimate.

substituent constant can be appreciably solvent dependent.^{17,18} One notes immediately that 1 has three methoxy groups whose interaction with the ring can be perturbed by solvation, as opposed to only one in 2. Another factor to be considered is that the 4-methoxy substituent in 1 is flanked by two ortho-substituents, which will tend to give a steric hindrance to its solvation not present in 2. For example, in nitromethane, a cyano group present as a substituent in 1,3,5-trimethylbenzene

(mesitylene) requires, to describe its influence on aromatic bromination, a σ^+ value of 0.686 rather than the usual 0.562. This was readily explained by the flanking methyl group giving an appreciable hindrance to a solvation, which moderates the electron-withdrawal by the meta-cyano group.19,20

In the present situation, steric hindrance to solvation of the 4-methoxy group present in 1 should lead to a faster ionisation reaction, contrary to observation, and this cannot be the



Fig. 2 Plot of log (k/k_o) for solvolyses of 3,4,5-trimethoxybenzoyl chloride (1) in 31 solvents at 25.0 °C against (0.32 N_T + 0.54 Y_{Cl}). Solvents: E, EtOH–H₂O; M, MeOH–H₂O; A, Acetone–H₂O; TFE, TFE–H₂O; HFIP, HFIP–H₂O; T–E, TFE–EtOH.

dominant influence of the introduction of the flanking 3,5-dimethoxy groups. An effect is needed which is modest in ethanol and appreciable in aqueous-fluoroalcohols, with the other solvents intermediate. Also, it is necessary to rationalise why the major influence on the specific rates is reflected entirely in a reduction of the sensitivity to changes in solvent ionising power (m-value), with essentially no change in the *l*-value. It appears that the transition state must involve about the same degree of nucleophilic solvation but a reduced heterolysis of the carbon-chlorine bond. Possibly, the expected variations in solvation at the methoxy groups are, in the absence of acidic solvents, secondary factors which change in intensity only slightly in going from initial state to transition state, and the dominant influence is indeed a tightening of the transition state (reduced bond-breaking) and reduced specific rates due to the electron-withdrawing influence of the methoxy groups $(\sigma = 0.115; \sigma^+=0.047)$.¹⁹ Interaction of fluoroalcohol molecules with the *meta*-methoxy groups of 1 will increase their electron- withdrawing power and increase the retardation relative to the corresponding solvolyses of 2. At the opposite extreme of the substitutent effects for 2 relative to 1, in ethanol, methanol, and 90% ethanol, there are indications (points lie above the plot in Fig. 2) for the superimposition of a bimolecular component to the solvolyses of 1 in these solvents. In a previously reported analysis,8 a good two-term Grunwald-Winstein analysis was obtained over all 37 solvents studied for 2. This analysis is, however, improved if these three solvents are omitted, with the F-test value rising from 630 to 971. A corresponding removal from the 40 solvent correlation, involving addition of 97% HFIP, CH₃COOH, and HCOOH⁶, leads to an increase in the F-test values from 772 to 1229 (Table 2). The component going by the addition-elimination pathway, with the addition step rate determining, in these solvents of relatively high nucleophilicity and relatively low ionising power, would be *favoured* by the presence of the electronwithdrawing *meta*-methoxy groups of **1**, and the overall effect would be a reduced ratio for the specific rates of **2** relative to those of **1**, as is observed (Table 1).

The lower specific rates allow an extension, at 25.0 °C, to aqueous HFIP binary solvents. One can either use the solvolyses of **1** as a substitute for the solvolyses of **2**, if one wishes to extend the solvent range for log (k/k_o) values for direct linear free energy relationship (LFER) plots, or one could use an extension of Figure 1 to estimate, the log (k/k_o) value for a given solvent for **2** from the value obtained experimentally for **1** and continue to use the solvolyses of **2** as the standard set of solvolyses for use in probing the solvolyses of other acyl chloride substrates.

It was established that, consistent with a previous observation²¹ for 2,6-dibromobenzoyl chloride, the solvolyses of 2,6-dichlorobenzoyl chloride (**3**) are slow at 25.0 °C and a temperature of 55.0 °C was found to be a convenient one for following the kinetics over a wide range of solvents.⁷ The same temperature has been found to be convenient for the study of the solvolyses of 2,4,6-trichlorobenzoyl chloride (**5**) and the specific rates are reported in Table 1, together with the corresponding ratios of the specific rates relative to those for **3** [k(5)/k(3)].

These specific rate ratios were found in TFE, six TFE–H₂O mixtures and three HFIP–H₂O mixtures to be essentially constant at 0.244 \pm 0.013 for the 10 solvents. This value is consistent with the belief⁷ that the solvolyses involve a unimolecular ionisation to an acylium ion. The electron-withdrawing *para*-chloro substituent ($\sigma = 0.227$; $\sigma^+ = 0.114$)¹⁹ when introduced into **3** would be expected to cause a modest retardation, as is observed. A two point determination based on hydrogen or chloro in the *para* position (**3** and **5**) leads to values for ρ of -2.7 and for ρ^+ of -5.4. The ρ^+ value is comparable with

tabulated values¹⁹ of -4.1 to -4.6 for solvolyses of benzhydryl chlorides and of -4.5 to -4.6 for solvolyses of *tert*-cumyl (2-phenyl-2-propyl) chloride in ethanol or aqueous acetone.

Closer in character to the present study is the finding by Bender and Chen ²² of a ρ^+ value of -3.9 for the solvolyses of a series of *para*-substituted 2,6-dimethylbenzoyl chlorides in 99% acetonitrile -1% water (by volume).

In TFE–ethanol mixtures, the k(5)/k(3) ratios rise modestly from 0.24 in TFE to values of 0.27, 0.33, and 0.34 with 20% increments in the ethanol content (by volume). In mixtures of ethanol, methanol, or acetone with water, with a 40% water content, ratios of 0.42, 0.40, and 0.48, respectively, are obtained. These values are also consistent with the electronwithdrawing influence of the 4-chloro substituent on an ionisation mechanism. As the alcohol content increases so also does the value for the ratio and in three instances it exceeds unity: 1.76 for 100% ethanol, 1.08 for 90% ethanol, and 1.27 for 80% acetone, indicating that, in these instances, the 4-chloro is very modestly favouring reaction. We will return to these observations after a consideration of the Grunwald–Winstein treatment using Eqn (1).

The results from the application of Eqn (1) are shown in Table 2 and the details of the correlation using the 27 data points are shown in Fig. 3. An analysis only using solvent ionising power (Eqn (1) without the lN_T term) gives a poor correlation with a slope of (*m* value) of 0.42 ± 0.04 and a correlation coefficient of 0.895. The correlation is considerably improved when the full equation is used with an *l* value of 0.28 ± 0.08 , *m* value of 0.62 ± 0.07 , and *c* value of 0.05 ± 0.08 (multiple correlation coefficient of 0.931). The *l* and *m* values are little changed from those for 2,6-dichlorobenzoyl chloride,⁷ which are also shown in Table 2.

A comparison of Fig. 3 with the Fig. 1 of the earlier publication ⁷ concerning the solvolyses of 2,6-dichlorobenzoyl chloride shows an almost identical pattern as regards the deviations from the best-fit correlation line. In particular, in both instances, the points for the solvolysis in 100% ethanol, 90% ethanol, 100% methanol and 90% methanol lie considerably above the correlation lines. Behaviour of this type can be an indication of the superimposition of an appreciable contribution from an alternative pathway in these solvents. Since these are solvents of relatively high nucleophilicity and relatively low ionising power, a bimolecular mechanism, such as in Scheme 2, is the most likely candidate.

Supporting the incursion of an addition-elimination mechanism in these solvents is the observation by Bender and Chen²² that, in their study of the hydrolysis of para-substituted 2,6-dimethylbenzoyl chlorides, addition of tetramethylammonium hydroxide led to the dominant pathway involving a bimolecular attack by hydroxide ion, with a ρ value of +1.2. This is consistent with the ρ value of +1.6 found²³ for the ethanolyses of a series of para and meta-substituted benzoyl chlorides, except that the *p*-methoxy derivative lies above the plot. In the present case, we have not increased the nucleophilicity of the attacking species²² but we have reduced, by replacement of methyl-substituents by chloro-substituents, the ability of the substrate to follow the ionisation pathway. Both approaches would increase the possibility for a detectable component from the addition-elimination pathway. Although a recent publication has proposed (based on density functional theory computations) that, for acetyl, chloroacetyl, or benzoyl chloride solvolyses, a concerted one-step S_N2 mechanism with a variable transition state structure operates, ²⁴ we continue to favour a combination of the two pathways of Scheme 1 (with nucleophilic solvation) and Scheme 2 (with general base catalysis).

With the four deviating points mentioned above omitted, new Grunwald–Winstein correlations [Eqn (1)] were carried out not only for **5** but also for **3**. These new correlations are included in Table 2 and, also, a new plot corresponding to this correlation of the solvolysis of **5** in 23 solvents, is presented in Fig. 4. The correlations are considerably improved and the sensitivity values (l and m) and the intercepts (c) are used to calculate values for specific rates of solvolyses proceeding by



Fig. 3 Plot of log (k/k_o) for solvolyses of 2,4,6-trichlorobenzoyl chloride (5) in 27 solvents at 55.0 °C against (0.29 $N_{\rm T}$ +0.62 $Y_{\rm CI}$). Solvents: E, EtOH–H₂O; M, MeOH–H₂O; A, Acetone–H₂O; TFE, TFE–H₂O; HFIP, HFIP–H₂O; T–E, TFE–EtOH.



Fig. 4 Plot of $\log(k/k_o)$ for solvolyses of 2,4,6-trichlorobenzoyl chloride (5) in 23 solvents at 55.0 °C against (0.40 N_{T} + 0.82 Y_{CI}). Solvents: E, EtOH–H₂O; M, MeOH–H₂O; A, Acetone–H₂O; TFE, TFE–H₂O; HFIP, HFIP–H₂O; T–E, TFE–EtOH (100E, 90E, 100M, 90M are omitted from the correlation; they are added to the plot to show the extent of their deviations.)

the ionisation mechanism. These are expressed below as the percentage contribution of this pathway to the overall experimental specific rate for the four omitted solvents. For **5**, the percentages of overall reaction calculated as proceeding by the ionisation mechanism are 5% in 100% ethanol, 10% in 100% methanol, 26% in 90% ethanol and 22% in 90% methanol. The corresponding values for **3** in 26 solvents are 13% for 100% ethanol, 14% for 100% methanol, 49% for 90% ethanol and 27% for 90% methanol. The contributions from the ionisation pathway are somewhat larger for **3** than for **5** because the introduction of the *para*-chloro substituent will, as indicated by literature ρ values from related Hammett correlations, slightly retard the ionisation pathway.^{22,23,25}

The kinetic measurements at 55.0 °C for solvolyses of **5** can also be compared with those⁷ for 2,4-dichlorobenzoyl chloride **4**. In aqueous ethanol, methanol, and acetone with less than 50% water content, **4** reacts faster than **5** (solubility problems prevent studies in more aqueous mixtures). These observations are, however, strongly reversed for solvolyses in water–fluoroalcohol mixtures.

We have shown previously⁷ that an analysis of specific rates for solvolysis of **4** at 55.0 °C in terms of Eqn (1) leads to a pronounced duality of mechanism, with 21 solvents favouring the addition–elimination pathway (Scheme 2) and the ten aqueous-fluoroalcohol solvents favouring the ionisation pathway (Scheme 1). The details are included in Table 2. This is consistent with a considerably lower steric hindrance to nucleophilic attack with only one *ortho*-substituent. For **5**, in the presence of the second *ortho*-substituent, the majority of the solvents now solvolyse with the ionisation pathway being dominant.

Conclusions

In ethanol, the 3,4,5-trimethoxybenzoyl chloride (1) reacts marginally slower than 4-methoxybenzoyl chloride (2). The extent to which 2 is favoured increases as water is added and the rate ratio favouring 2 increases to a value of about 35 in 97-70% TFE. A direct linear free energy relationship (LFER) correlation of log (k/k_o) for 1 against log (k/k_o) for 2 gives a reasonably linear plot with a slope of 0.61 ± 0.05 . An extended Grunwald–Winstein treatment (Eqn (1)) of the specific rates of solvolysis of 1 shows that it has essentially the same l value as for solvolyses for 2,8 and the source of the differences in behaviour lies in very different m values of 0.54 (±0.04) for 1 and $0.81 (\pm 0.02)$ for 2. It is suggested that the dominant influence differentiating the behaviour of 1 and 2 is a tightening of the transition state due to the electron-withdrawing influence of the two meta-methoxy groups. The lower specific rates for 1 allow an extension to direct measurements in HFIP-H₂O solvents at 25.0 °C. These values could not be obtained^{2,6} earlier due to a fast reaction of 2. Use of 1 as the substrate extends the range of solvents which can be used in LFER correlation of related solvolyses against log (k/k_o) for para-substituted methoxybenzoyl chlorides.

The 2,4,6-trichlorobenzoyl chloride (5) reacts, at 55.0 °C, about one quarter as fast as 2,6-dichlorobenzoyl chloride 3 in 100% TFE, 97-50% TFE–H₂O, and 97–70% HFIP–H₂O (Table 1). The differences become smaller in pure alcohols and in mixtures of water with ethanol, methanol, or acetone and in 100% and 90% ethanol, and in 80% acetone, the solvolyses of 5 are marginally faster than of 3. It is proposed that, due to the steric hindrance from the *ortho*-substituents, in the majority of solvents the ionisation pathway (Scheme 1) is dominant for both 3 and 5 but in solvents of low ionising power and relatively high nucleophilicity an appreciable contribution from the addition–elimination pathway (Scheme 2) is operative.

Comparing the calculated specific rates, using the l and m values from entries 4 and 8 of Table 2, with the experimental values, the percentages of reaction proceeding with ionisation have been estimated for both **3** and **5** in 100% and 90% ethanol, and in 100% and 90% methanol.

Experimental

The 3,4,5-trimethoxybenzoyl chloride (1, 98%) and the 2,4,6-trichlorobenzoyl chloride (5, 97%) were obtained from Sigma-Aldrich Chemical Company and they were used as received. Solvents were purified as described previously.¹¹ The determination of the kinetics of the solvolysis reactions ⁷ and the calculation of the specific rates of solvolysis^{7,26} were as previously reported.

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