

# Correlation of the rates of solvolysis of 2-furancarboxyl chloride and three naphthoyl chlorides

Malcolm J. D'Souza,<sup>1\*</sup> Mary E. Boggs<sup>1</sup> and Dennis N. Kevill<sup>2</sup>

<sup>1</sup>Department of Chemistry, Wesley College, 120 N. State Street, Dover, Delaware 19901-3875, USA

<sup>2</sup>Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115-2862, USA

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**ABSTRACT:** The correlations of the specific rates of solvolysis of the title compounds using extended forms of the Grunwald–Winstein equation are consistent with the overall picture which is emerging for acyl chloride solvolyses, with competing addition–elimination (with rate-determining addition) and ionization (assisted by nucleophilic solvation) pathways. Except in the more ionizing solvents of low nucleophilicity, 2-furancarboxyl chloride follows the addition–elimination pathway, in contrast to 2-thiophenecarboxyl chloride. Except in solvents of highest nucleophilicity and low ionizing power, the solvolyses of the naphthoyl chlorides (1-naphthoyl, 2-naphthoyl and 6-methyl-2-naphthoyl) all favor the ionization pathway. In the correlation of the 1-naphthoyl chloride solvolyses, there is a slight improvement when a term governed by the sensitivity to changes in the aromatic ring parameter ( $hI$ ) is incorporated; this can be associated with a rather minor steric hindrance involving the *peri*-hydrogen. Copyright © 2006 John Wiley & Sons, Ltd.

**KEYWORDS:** extended Grunwald–Winstein equation; solvolysis; 2-furancarboxyl chloride; naphthoyl chlorides

## INTRODUCTION

In correlation analyses of the specific rates of solvolysis of benzoyl chloride and several *meta*- and *para*-substituted derivatives, we previously obtained very good correlations with the application of the equation

$$\log(k/k_0) = lN_T + mY_{Cl} + c \quad (1)$$

and the recognition of two pathways, believed to involve ionization and addition–elimination.<sup>1</sup> In Eqn (1),  $k$  and  $k_0$  are the specific rates of solvolysis in a given solvent and in the standard solvent (80% ethanol), respectively,  $l$  is the sensitivity towards changes in solvent nucleophilicity ( $N_T$ ),<sup>2–4</sup>  $m$  is the sensitivity towards changes in solvent ionizing power ( $Y_{Cl}$  for a chloride-ion leaving group)<sup>5,6</sup> and  $c$  is a constant (residual) term. The  $N_T$  scale was developed based on the specific rates of solvolysis of the *S*-methylthiophenium ion. The large neutral leaving group (dibenzothiophene) leads to leaving-group effects being negligible, in contrast to initially neutral substrates which eject an anionic leaving group, with appreciable changes in the leaving-group effects upon varying the solvent. The  $Y_X$  scales are based on the

solvolyses of adamantyl derivatives, where nucleophilic solvent assistance is sterically hindered.

It has been known for some time<sup>7</sup> that the severe steric hindrance accompanying the introduction of two *ortho*-substituents can cause a change in the mechanism of nucleophilic substitution from addition–elimination to ionization, and this was observed in a study of the solvolyses of 2,6-dimethylbenzoyl chloride.<sup>8</sup> Correlation analysis of these solvolyses was best carried out<sup>1</sup> with incorporation of a term governed by the sensitivity  $h$  to changes in the aromatic-ring parameter ( $I$ ),<sup>9,10</sup> using the equation

$$\log(k/k_0) = lN_T + mY_{Cl} + hI + c \quad (2)$$

The  $I$  scale can be considered as a measure of the changes in the interaction of the solvent with aromatic rings present in the substrate on proceeding to the positively charged incipient carbocation of the transition state. The scale was developed from a consideration of the differential solvation effects on the specific rates of solvolysis of the *p*-methoxybenzyltrimethylsulfonium ion and the 1-adamantyltrimethylsulfonium ion.

In attempts to correlate the solvolyses of several benzoyl chlorides,<sup>8</sup> Liu and co-workers recommended the use of a solvent ionizing power scale based on the solvolyses of 2-chloro-2-(3'-chlorophenyl)adamantane ( $Y_{BnCl}$ ), devised to apply to situations with one aromatic ring attached to the  $\alpha$ -carbon.<sup>11</sup> Use of this scale is an

\*Correspondence to: M. J. D'Souza, Department of Chemistry, Wesley College, 120 N. State Street, Dover, Delaware 19901-3875, USA.

E-mail: dsouzama@wesley.edu

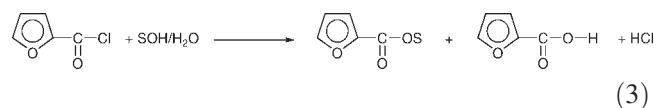
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alternative to the use of  $mY_{Cl}$  in conjunction with  $hI$  and it involves the assumption of an  $h/m$  ratio of close to 1.<sup>9,12</sup> for the solvolyses under study. Unsurprisingly, for the solvolyses of *meta*- and *para*-substituted benzoyl chlorides (where the  $hI$  term is negligible), the analyses<sup>8</sup> incorporating  $Y_{BnCl}$  were uniformly inferior to those using Eqn (1).<sup>1</sup>

There have been two recent analyses of the specific rates of solvolysis of naphthoyl chlorides. The earlier<sup>13</sup> was limited to 1-naphthoyl chloride and 2-naphthoyl chloride and the other<sup>14</sup> also included two substituted naphthoyl chlorides. In the earlier publication the analyses are in terms of Eqn (2) and in the other both the  $Y_{BnCl}$  scale<sup>11</sup> and another solvent ionizing power scale ( $Y_{xBnCl}$ ), based on the solvolyses of  $\alpha$ -*tert*-butyl(2-naphthoyl)methyl chloride,<sup>15</sup> were used, either alone or in conjunction with  $N_{OTs}$  values<sup>2,16</sup> (based on solvolyses of methyl *p*-toluenesulfonate) within Eqn (1). Both reports indicate an appreciable influence on the specific rates of solvolysis upon introduction of the added fused ring.

With a combination of specific rate values from these two publications, we have been able to carry out extended Grunwald–Winstein analyses for three of the four substrates studied (the fourth was not studied in sufficient solvents). These allow a more thorough consideration of the extent to which the change from benzoyl to naphthoyl chlorides requires the incorporation of the  $hI$  term (or replacement of  $Y_{Cl}$  values by  $Y_{BnCl}$  or  $Y_{xBnCl}$  values).

Recently, we showed<sup>17</sup> that the solvolyses of 2-thiophenecarbonyl chloride [**1a**, structure as for reactant in Eqn (3), but with the O of the ring replaced by S] followed a pathway involving ionization assisted by nucleophilic solvation<sup>2,18</sup> for all but the solvents of highest nucleophilicity and lowest ionizing power



This was in contrast to previous claims of an  $S_N2$  process.<sup>19,20</sup> The specific rates of solvolysis of 2-furancarboxyl chloride [**1b**; Eqn (3)] were initially claimed<sup>19</sup> to follow an  $S_N2$  process, but this was later modified to the claim<sup>20</sup> of an addition–elimination (association–dissociation) pathway. The nucleophilic solvation involves stabilization of the incipient carbocation by an ion–dipole interaction with a nucleophilic (rather than electrophilic) center in the solvent molecules. In this work, we expanded the study of the solvolyses of **1b** from the previously studied aqueous ethanol, aqueous methanol and aqueous acetone mixtures to solvents with an appreciable fluoro alcohol component. The aim was to look for a solvent-induced changeover in mechanism from the previously reported addition–elimination to the ionization which was favored for the solvolyses of **1a** in a majority of the solvents studied. Also, the claims for

important differential solvation effects at the aromatic rings on going to the transition state could be investigated in terms of the magnitude of the sensitivity ( $h$ ) to changes in  $I$  value.

These studies of acylation mechanisms will lead to a better understanding of the pathways involved in the acylation of the hydroxyl groups of potential pharmaceuticals to increase their water solubility. For example, acylation of taxol using **1a** or **1b** substantially increases its very low water solubility.<sup>21</sup>

## RESULTS AND DISCUSSION

The specific rates of solvolysis of **1b** were measured at 25.0 °C in a variety of solvents, mainly containing a fluoro alcohol component. The data are presented in Table 1.

The new data were combined with literature data<sup>19,20</sup> and, together with appropriate  $N_T$  values<sup>2–4</sup> and  $Y_{Cl}$  values,<sup>5,6</sup> were analyzed using Eqn (1). Values from the correlation analyses are reported in Table 2. Initially, all of the specific rates of solvolysis for which both  $N_T$  and  $Y_{Cl}$  values are available were included in the correlation (Fig. 1). The sensitivity values obtained (1.17 for  $l$  and 0.47 for  $m$ ) appear, in isolation, to suggest a concerted ( $S_N2$ ) pathway. However, inspection of the plot indicates that the solvents with high fluoro alcohol content [100 and 97% 2,2,2-trifluoroethanol (TFE) and 90% 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)] and, therefore, of low nucleophilicity and high ionizing power, lie above the plot. This suggests the frequently observed<sup>1</sup> incursion of an ionization pathway for the solvolyses in these solvents. Appreciable changes observed upon removal of these three data points (second entry in Table 2) show that, despite its reasonable multiple correlation coefficient and  $F$ -test value, the original correlation was not robust and sensitivity values are now obtained which

**Table 1.** Specific rates of solvolysis ( $k$ ) of 2-furancarboxyl chloride (**1b**) at 25.0 °C

Solvent	$10^5 k$ (s <sup>-1</sup> )	Solvent	$10^5 k$ (s <sup>-1</sup> )
100% EtOH	13.7 ± 0.4 <sup>c</sup>	90% HFIP <sup>b</sup>	0.286 ± 0.016
80% EtOH <sup>a</sup>	47.8 ± 1.5 <sup>d</sup>	80T–20E <sup>a,e</sup>	1.01 ± 0.01
100% TFE	0.111 ± 0.009	60T–40E <sup>a,e</sup>	2.73 ± 0.10
97% TFE <sup>b</sup>	0.109 ± 0.007	40T–60E <sup>a,e</sup>	7.42 ± 0.19
70% TFE <sup>b</sup>	3.06 ± 0.08	20T–80E <sup>a,e</sup>	12.1 ± 0.5
50% TFE <sup>b</sup>	13.1 ± 0.6		

<sup>a</sup> Volume/volume basis at 25.0 °C.

<sup>b</sup> Weight/weight basis.

<sup>c</sup> Previous value of 15.9.<sup>20</sup>

<sup>d</sup> Previous values of 41.3<sup>19</sup> and 44.7.<sup>20</sup>

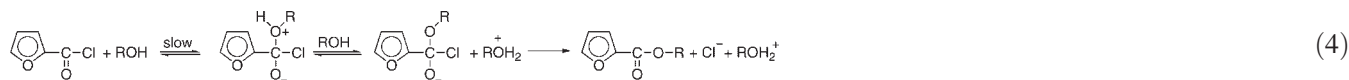
<sup>e</sup> T–E are TFE–ethanol mixtures.

**Table 2.** Coefficients from extended Grunwald–Winstein treatments [Eqn (1)] of the solvolyses of 2-furancarboxyl chloride (**1b**) at 25.0 °C and a comparison with coefficients from the correlations for other acyl chlorides

Substrate	$n^a$	$\rho^b$	$m^b$	$c^b$	$R^c$	$F^d$	$\alpha^e$
<b>1b</b>	38 <sup>f</sup>	1.17 ± 0.06	0.47 ± 0.03	0.07 ± 0.07	0.959	202	0.28
	35 <sup>g</sup>	1.61 ± 0.11	0.58 ± 0.03	0.17 ± 0.06	0.951	152	0.22
	33 <sup>h</sup>	1.73 ± 0.14	0.60 ± 0.04	0.19 ± 0.06	0.947	131	0.22
	29 <sup>i</sup>	1.75 ± 0.15	0.60 ± 0.04	0.20 ± 0.06	0.946	111	0.23
	23 <sup>j</sup>	1.76 ± 0.15	0.59 ± 0.05	0.21 ± 0.06	0.947	87	0.23
	17 <sup>k</sup>	1.72 ± 0.15	0.55 ± 0.05	0.19 ± 0.07	0.951	66	0.23
<b>1a</b> <sup>l</sup>	35	0.65 ± 0.04	0.86 ± 0.02	0.04	0.990	754	0.18
PhOCOCl <sup>m</sup>	21	1.68 ± 0.10	0.57 ± 0.06	0.12	0.973	159	0.41
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCl <sup>n</sup>	34	1.78 ± 0.08	0.54 ± 0.04	0.11	0.969	237	0.37

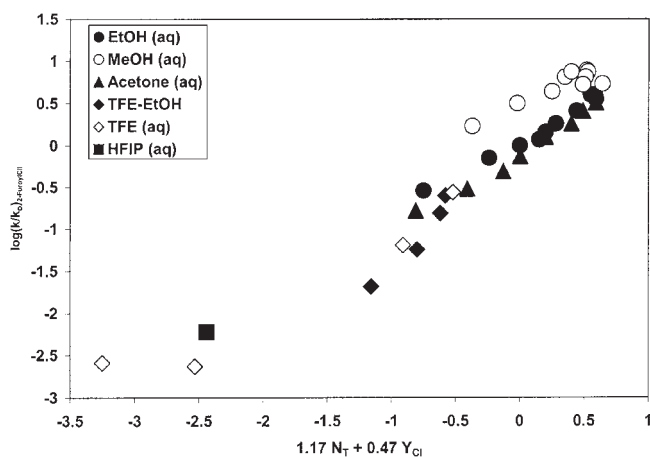
<sup>a</sup> Number of data points.<sup>b</sup> With associated standard errors.<sup>c</sup> Multiple correlation coefficient.<sup>d</sup> *F*-test value.<sup>e</sup> Standard error of the estimate.<sup>f</sup> Using the specific rates of solvolysis from Table 1 and additional solvent systems from Ref. 20.<sup>g</sup> With 100 and 97% TFE and 90% HFIP removed.<sup>h</sup> Data for 100% TFE and all fluoro alcohol–water mixtures removed.<sup>i</sup> All listed under footnote h plus 100% H<sub>2</sub>O, 10% EtOH, 10% MeOH, 10% acetone removed.<sup>j</sup> All listed under footnote i plus 30%, 20% EtOH, 30%, 20% MeOH, 30%, 20% acetone removed.<sup>k</sup> All listed under footnote j, plus 50 and 40% EtOH, 50 and 40% MeOH, 50% and 40% acetone removed.<sup>l</sup> From Ref. 17 (with omission of 100 and 90% EtOH, 100 and 90% MeOH, 90% acetone).<sup>m</sup> From Ref. 23 (all solvents).<sup>n</sup> From Ref. 1 (all solvents except 97% HFIP).

are typical of an addition–elimination mechanism with addition rate-determining [Eqn (4)].



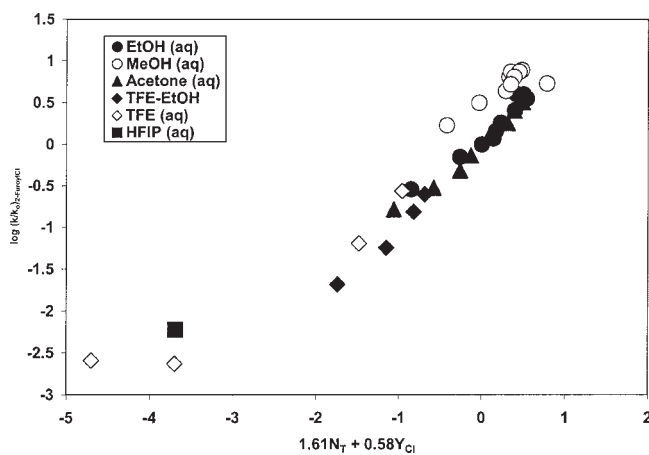
Although the standard error of the estimate is somewhat reduced, so also are the multiple correlation coefficient and the *F*-test value (fewer data points). The revised correlation is shown in Fig. 2, with the excluded data points added to show their appreciable deviation.

It can be seen from Figs 1 and 2 that the removal from the correlation of these three data points at the extreme left reduces by about 50% the range of abscissa values covered, impacting the goodness-of-fit parameters. The

**Figure 1.** Plot of  $\log(k/k_0)$  for solvolyses of 2-furancarboxyl chloride at 25.0 °C against  $1.17N_T + 0.47Y_{Cl}$ 

comparison of the first two entries in Table 2 provides a good example of the observation by Bentley *et al.*<sup>22</sup> that

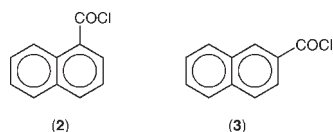
multiparameter treatments tend to average out the values and obscure any changes in the sensitivity values that might occur within the range of the data being subjected to correlation analysis. Tests involving the robustness of the data are strongly recommended. As can be seen from Table 2, continuing the removal of data points in a sequence where the solvents will increasingly favor a

**Figure 2.** Plot of  $\log(k/k_0)$  for solvolyses of 2-furancarboxyl chloride at 25.0 °C against  $1.61N_T + 0.58Y_{Cl}$ . The points for 90% HFIP, 100% TFE and 97% TFE are not included in the correlation; they are added to the figure to show their substantial deviation

bimolecular pathway produces only very minor perturbations (except, of course, for the associated reductions in the *F*-test value). This indicates that the correlation has become robust and the addition–elimination pathway is dominant for all of the solvents except for the three of highest fluoro alcohol content. This is in marked contrast to the solvolyses of 2-thiophenecarbonyl chloride (sulfur replacing oxygen, **1a**), which involve very different *l* and *m* values (Table 2) and which proceed by an ionization pathway in all but solvents of high nucleophilicity and low ionizing power.<sup>17</sup> These findings parallel those observed upon sulfur-for-oxygen substitution in the solvolyses of phenyl chloroformate,<sup>23</sup> with one replacement leading to a delicate balance between the two mechanisms<sup>24,25</sup> and replacement of both oxygen atoms leading to a changeover from a dominant addition–elimination pathway to a dominant ionization pathway.<sup>25</sup>

In the solvolyses of benzoyl chlorides, a perturbation leading to a meaningful contribution from the *hl* term [use of Eqn (2)] was found only for the sterically hindered solvolyses of 2,6-dimethylbenzoyl chloride.<sup>1</sup> Claims<sup>8</sup> for improved correlations using  $Y_{\text{BnCl}}$  and  $N_{\text{OTs}}$  values within Eqn (1) result from the neglect of the mechanistic variation induced by changes in solvent and, possibly, from a fortuitous cancellation of the deviations involved in the use of  $N_{\text{OTs}}$  and  $Y_{\text{BnCl}}$  scales. Perturbations due to aromatic rings are more likely to be observed in correlations of the specific rates of solvolysis of naphthoyl chlorides. It is well established that the greater is the number of aromatic rings capable of conjugation with an electron-deficient  $\alpha$ -carbon, the larger are the perturbations<sup>9,15,26,27</sup> and, for the 1-naphthoyl chlorides, there is the possibility of steric hindrance to the approach of the solvent to the  $\alpha$ -carbon due to the *peri*-hydrogen (on C-8) effect.<sup>13,14</sup>

Values are available, at 25.0 °C, for the specific rates of solvolysis of 1-naphthoyl chloride (**2**), 2-naphthoyl chloride (**3**), 4-methyl-1-naphthoyl chloride (**4**) and 6-methoxy-2-naphthoyl chloride (**5**). Unfortunately, the solvolyses of **4** have not been studied in a sufficient number of solvents and the correlation analyses in terms of Eqns (1) and (2) could be carried out only for **2**, **3** and **5**. These correlations are reported in Table 3, together with data for comparison from previous correlations<sup>1</sup> of the specific rates of *p*-methoxybenzoyl chloride (**6**) and 2,6-dimethylbenzoyl chloride (**7**) solvolyses.



The initial correlations are for all the specific rates of solvolysis for which both  $N_{\text{T}}$  and  $Y_{\text{Cl}}$  values are available and of all the specific rates (one fewer) for which  $N_{\text{T}}$ ,  $Y_{\text{Cl}}$  and *I* values are all available. Moderately good correlations are obtained but, from inspection of the plots, it is

clear that, as with the majority of the benzoyl chloride solvolyses, a change in mechanism is occurring. For the solvolyses of **2** and **5**, only the more extreme of the solvents previously shown<sup>1</sup> to favor addition–elimination (100 and 90% EtOH; 100 and 90% MeOH; 90% acetone) deviate appreciably from the plots and all three correlations were considerably improved after omission of the data for solvolyses in these solvents, resulting in *l* and *m* values typical for an ionization mechanism with accompanying nucleophilic solvation.<sup>2,18a</sup> For the solvolyses of **3**, a further, but less pronounced, improvement was observed when further data points were removed, and these changes are sufficiently minor for the correlation to be considered as robust after the initial five data points were removed.

The specific rates of solvolysis were taken from two publications which appeared almost simultaneously.<sup>13,14</sup> There is considerable overlap and the agreement between the values is usually acceptable. There are a few examples of poor agreement, however, most noticeably one value being higher than the other by 92% for **2** and 50% for **3** in 90% acetone and by 47% for **2** in 90% methanol. Fortunately, both of the solvents involved are within the five which are excluded from the correlation of the specific rates of solvolysis limited to the ionization pathway. When two specific rate values are available, we used the value from the paper with the earlier reception date.<sup>13</sup> The overall data set is most extensive for **3**, with studies in aqueous TFE and HFIP<sup>13</sup> being augmented by studies in TFE–ethanol mixtures.<sup>14</sup>

A major feature of our correlations of the specific rates of solvolysis of **3** and **5** is that, with use of Eqn (2), the initial weak evidence for a minor contribution from the *hl* term (*h* values of  $0.33 \pm 0.24$  and  $0.33 \pm 0.25$ , respectively) disappears when the five solvents favorable towards addition–elimination are omitted (*h* values of  $0.00 \pm 0.23$  and  $0.11 \pm 0.20$ ), suggesting one possible reason why the previous studies indicated an appreciable *h* value<sup>13</sup> or, the equivalent, preferable use of  $Y_{\text{BnCl}}$  or  $Y_{\text{XBNCl}}$ .<sup>14</sup>

The small *h* values are not unexpected<sup>1</sup> because the dominant resonance contribution proposed for the benzoyl cation<sup>28</sup> will also be operative for the naphthoyl cation [Eqn (5)], with the positive charge substantially transferred within the carbonyl group from the carbon to the oxygen.



For the specific rates of solvolysis of **2**, parallel correlations to those carried out for **3** and **5** lead to a larger *h* value. The value is  $0.77 \pm 0.25$  with all solvents included, which falls to  $0.54 \pm 0.23$  when the five solvents are omitted (Table 3). This is consistent with the previous suggestion<sup>13,14</sup> that steric hindrance to the approach to the carbonyl carbon from the *peri*-hydrogen influences the mechanism and with the observation for

**Table 3.** Correlation<sup>a</sup> of the specific rates of solvolysis<sup>b</sup> of 1-naphthoyl chloride (**2**), 2-naphthoyl chloride (**3**) and 6-methoxy-2-naphthoyl chloride (**5**) and a comparison with values from correlations involving benzoyl chlorides

Substrate	Scales	$n^c$	$l^d$	$m^d$	$h^d$	$c^d$	$R^e$	$F^f$
<b>2</b>	$N_T, Y_{Cl}$	20 <sup>g</sup>	$0.17 \pm 0.11$ (0.163)	$0.62 \pm 0.07$		$0.12 \pm 0.09$	0.925	51
	$N_T, Y_{Cl}, I$	20 <sup>g</sup>	$0.28 \pm 0.10$ (0.013)	$0.67 \pm 0.06$	$0.77 \pm 0.25$ (0.008)	$0.11 \pm 0.08$	0.953	53
	$N_T, Y_{Cl}$	15 <sup>h</sup>	$0.18 \pm 0.09$ (0.080)	$0.78 \pm 0.09$		$-0.11 \pm 0.10$	0.944	49
<b>3</b>	$N_T, Y_{Cl}, I$	15 <sup>h</sup>	$0.29 \pm 0.09$ (0.009)	$0.83 \pm 0.08$	$0.54 \pm 0.23$ (0.037)	$-0.10 \pm 0.09$	0.963	47
	$N_T, Y_{Cl}$	32 <sup>i</sup>	$0.31 \pm 0.07$	$0.51 \pm 0.04$		$0.11 \pm 0.08$	0.921	81
	$N_T, Y_{Cl}, I$	31 <sup>j</sup>	$0.39 \pm 0.09$	$0.54 \pm 0.05$	$0.33 \pm 0.24$ (0.181)	$0.12 \pm 0.08$	0.923	52
	$N_T, Y_{Cl}$	27 <sup>h</sup>	$0.34 \pm 0.05$	$0.66 \pm 0.04$		$-0.22 \pm 0.07$	0.964	156
	$N_T, Y_{Cl}, I$	26 <sup>h,j</sup>	$0.38 \pm 0.07$	$0.68 \pm 0.05$	$0.15 \pm 0.18$ (0.424)	$-0.21 \pm 0.08$	0.963	94
	$N_T, Y_{Cl}$	15 <sup>k</sup>	$0.30 \pm 0.05$	$0.71 \pm 0.04$		$-0.45 \pm 0.11$	0.980	149
<b>5</b>	$N_T, Y_{Cl}, I$	14 <sup>j,k</sup>	$0.30 \pm 0.08$	$0.71 \pm 0.07$	$0.00 \pm 0.23$ (0.998)	$-0.45 \pm 0.14$	0.980	80
	$N_T, Y_{Cl}$	17 <sup>l</sup>	$0.23 \pm 0.10$	$0.48 \pm 0.07$		$0.10 \pm 0.08$	0.892	27
	$N_T, Y_{Cl}, I$	17 <sup>l</sup>	$0.29 \pm 0.11$	$0.52 \pm 0.08$	$0.33 \pm 0.25$ (0.206)	$0.09 \pm 0.07$	0.906	20
	$N_T, Y_{Cl}$	13 <sup>h</sup>	$0.29 \pm 0.07$	$0.66 \pm 0.08$		$-0.08 \pm 0.07$	0.946	43
	$N_T, Y_{Cl}, I$	13 <sup>h</sup>	$0.31 \pm 0.09$	$0.67 \pm 0.08$	$0.11 \pm 0.20$ (0.589)	$-0.07 \pm 0.07$	0.948	27
<b>6<sup>m</sup></b>	$N_T, Y_{Cl}$	37	$0.31 \pm 0.05$	$0.81 \pm 0.02$		$0.08 \pm 0.21^n$	0.989	738
<b>7<sup>m</sup></b>	$N_T, Y_{Cl}$	16	$0.41 \pm 0.29$ (0.173)	$0.85 \pm 0.08$		$0.21 \pm 0.31^n$	0.962	82
	$N_T, Y_{Cl}, I$	16	$0.34 \pm 0.15$ (0.040)	$0.89 \pm 0.04$	$0.92 \pm 0.15$	$0.15 \pm 0.16^n$	0.991	227

<sup>a</sup> Using Eqns (1) and (2); with two and three parameters, respectively.

<sup>b</sup> At 25.0 °C and specific rates of solvolysis, from Refs 13 and 14.

<sup>c</sup> Number of data points.

<sup>d</sup> With associated standard errors and (in parentheses) the probabilities that the contribution from the  $lN_T$ ,  $mY_{Cl}$  or  $hI$  term is statistically insignificant (if > 0.005).

<sup>e</sup> Multiple correlation coefficient.

<sup>f</sup>  $F$ -test value.

<sup>g</sup> All determinations with both  $N_T$  and  $Y_{Cl}$  values available, 16 from Ref. 13 and four from Ref. 14.

<sup>h</sup> With 100 and 90% EtOH, 100 and 90% MeOH and (not available for **5**) 90% acetone removed.

<sup>i</sup> All determinations with both  $N_T$  and  $Y_{Cl}$  values available, 27 from Ref. 13 and five from Ref. 14.

<sup>j</sup> No  $I$  value available for 30% CH<sub>3</sub>CN.

<sup>k</sup> Omitting 100–50% EtOH, 100–50% MeOH, 90–50% acetone.

<sup>l</sup> From Ref. 14.

<sup>m</sup> Correlation data from Ref. 1.

<sup>n</sup> Accompanied by the standard error of the estimate.

the benzoyl chloride systems of an appreciable  $hI$  term only when two *ortho*-methyl groups are present. The  $h$  value observed is appreciably less than the  $0.92 \pm 0.15$  obtained for the solvolyses of **7** (Table 3), consistent with a smaller steric effect from a *peri*-hydrogen than from two *ortho*-methyl groups.

A feature of the earlier publications was the claim by Liu *et al.*<sup>14</sup> that it would be preferable to use the  $Y_{xBnCl}$  scale<sup>15,27</sup> in conjunction with the  $N_{OTs}$  scale<sup>6,16</sup> for correlations in terms of Eqn (1). Development of similarity model scales can indeed be a useful way of reducing the number of terms needed in a linear free-energy relationship. However, the use of similarity models comes at a price and one must carefully observe the requirement of a fairly close similarity of the system under investigation to the standard system. This is, of course, the rationale given<sup>15</sup> for having both  $Y_{BnCl}$  and  $Y_{xBnCl}$  scales. The requirement for a valid similarity model ionizing power scale (to be used in place of  $Y_X$  plus  $I$  scales) is that the  $h/m$  ratio for the solvolyses under consideration should be very similar to (ideally, equal to) the  $h/m$  ratio for the solvolyses chosen as the similarity model.<sup>9</sup>

With a naphthyl group adjacent to developing positive charge, if a substantial part of this charge is relayed to the two aromatic rings,  $Y_{xBnCl}$  could well be the scale of choice. Liu *et al.* presented analyses using  $N_{OTs}$  in

conjunction with both  $Y_{BnCl}$  and  $Y_{xBnCl}$  and, although this aspect is not discussed in their paper, not only does  $Y_{xBnCl}$  not give substantially improved correlations but, for the three (of four) correlations with at least 14 data points, marginally better correlations are obtained with the  $Y_{BnCl}$  scale. Of course, since we can (using the values in Table 3) estimate  $h/m$  ratios of  $0.65 \pm 0.31$  for **2**,  $0.00 \pm 0.35$  for **3** and  $0.16 \pm 0.33$  for **5**, the real surprise is that  $Y_{xBnCl}$  does almost as good a job within the correlations as  $Y_{BnCl}$ . The very similar behavior ceases to be a surprise, however, when one looks at the correlations presented within the paper in which the  $Y_{xBnCl}$  scale was developed. An excellent correlation of  $Y_{xBnCl}$  against  $Y_{BnCl}$  was reported with a slope of  $0.96 \pm 0.03$  and a correlation coefficient of 0.993.<sup>15a</sup> From this, it is obvious, of course, that only very minor variations can result if  $Y_{xBnCl}$  values replace  $Y_{BnCl}$  values in a correlation and, accordingly, very little is to be gained from the introduction of the additional scale.

A correlation was also carried out,<sup>15a</sup> for 17 of the solvents studied, of  $Y_{xBnX}$  values against  $N_T$ ,  $Y_{Cl}$  and  $I$  values. A very small  $l$  value of  $0.12 \pm 0.11$  was accompanied by an  $m$  value of  $0.93 \pm 0.07$  and an  $h$  value of  $1.83 \pm 0.26$  ( $R = 0.982$ ). This leads to an  $h/m$  ratio of  $1.97 \pm 0.31$ , consistent with the involvement of two aromatic rings. Since the highest  $h/m$  ratio observed for

the naphthoyl chloride solvolyses is  $0.65 \pm 0.31$ , neither  $Y_{\text{BnCl}}$  nor  $Y_{\text{xBnCl}}$  will be appropriate similarity model scales, but the  $Y_{\text{BnCl}}$  scale associated with an  $h/m$  ratio of 1.79<sup>9,12</sup> will be very slightly preferable to the  $Y_{\text{xBnCl}}$  scale with an  $h/m$  ratio of 1.97.

## CONCLUSION

Replacing the sulfur of 2-thiophenecarbonyl chloride (**1a**) by the oxygen of 2-furancarboxyl chloride (**1b**) has a profound effect on the mechanism of solvolysis. In the majority of solvents, the sensitivity parameters ( $l = 0.65$ ;  $m = 0.86$ ) obtained for solvolyses of **1a**<sup>17</sup> are consistent with an ionization mechanism with assistance from nucleophilic solvation and, in the majority of solvents, the sensitivity parameters obtained in this study for solvolyses of **1b** ( $l = 1.73$ ;  $m = 0.60$ ) are consistent with an addition–elimination (association–dissociation) mechanism, with the addition step being rate-determining. For both solvolyses, it is possible by appropriate choice of solvents to switch over to the alternative mechanism.

Correlations of the solvolyses of naphthoyl chlorides have been proposed previously to be perturbed by the presence of the two aromatic rings, with incorporation of an  $hI$  term<sup>13</sup> or use of the  $Y_{\text{BnCl}}$  or  $Y_{\text{xBnCl}}$  scale<sup>14</sup> being a feature of the analyses. A more thorough treatment has been made possible by combining the specific rate data from the two publications. We find for 2-naphthoyl chloride (**3**) and its 6-methoxy derivative (**5**) that there is negligible sensitivity towards changes in the value of the  $I$  parameter ( $h$  values of  $0.00 \pm 0.23$  and  $0.11 \pm 0.20$ , respectively) and only for 1-naphthoyl chloride (**2**) is the incorporation of the  $hI$  term not statistically insignificant ( $h$  value of  $0.54 \pm 0.23$ , with a probability of 0.037 that the  $hI$  term is statistically insignificant). For **2**, there is a degree of steric hindrance due to the *peri*-hydrogen on C-8 and it may be, as with 2,6-dimethylbenzoic acid (**7**), that hindrance to nucleophilic solvation at the reaction site leads to an increased sensitivity toward changes in the solvation effects at the aromatic rings.

The use of either  $Y_{\text{BnCl}}$  ( $h/m$  of 1.8) or  $Y_{\text{xBnCl}}$  ( $h/m$  of 2.0) in the correlations of the three naphthoyl chlorides<sup>14</sup> will clearly not be appropriate when the  $h/m$  value for all of the solvolyses under consideration is lower than 0.6. Further, owing to their very similar  $h/m$  values, there does not seem to be any substantial advantage to having available both of the similarity model scales.

## EXPERIMENTAL

2-Furancarboxyl chloride (Aldrich, 2-furoyl chloride, 95%) was used without further purification. Solvents were purified and the kinetic runs carried out as described pre-

viously.<sup>3</sup> The multiple regression analyses were performed using commercially available statistical packages.

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