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Correlation of the rates of solvolysis of benzoyl chloride and derivatives using extended forms of the Grunwald–Winstein equation†

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ABSTRACT: Available specific rates of solvolysis at 25 °C of benzoyl chloride and four *para*-substituted derivatives for which both N_T and Y_{Cl} values are tabulated were analyzed using the extended (two-term) Grunwald–Winstein equation. The ionization pathway with appreciable nucleophilic solvation of the incipient carbocation observed for the *p*-methoxy derivative is accompanied by increasingly important regions of dominant operation of an addition–elimination pathway as the Hammett σ value for the substituent increases. Accordingly, for the *p*-nitro derivative only the 97% HFIP data point deviates from the addition–elimination correlation. Correlations of the specific rates of solvolysis of 2,6-dimethylbenzoyl chloride are improved by incorporation of a term governed by the aromatic ring parameter (*I*). Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: Grunwald–Winstein equation; solvolysis; solvent nucleophilicity; solvent ionizing power; aromatic ring parameter

INTRODUCTION

The Grunwald–Winstein equation:

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

was originally designed[1] to give a one-term linear free energy correlation against the specific rates of solvolysis of *tert*-butyl chloride, which was taken as a model for a solvolysis involving rate-determining ionization. It is now well established that solvolyses of *tert*-butyl chloride have a contribution from nucleophilic solvation of the developing cation.[2–4] Since many other solvolyses have a similar contribution, this is not necessarily a handicap if one wishes to carry out a one-term correlation and, for example, the specific rates of solvolysis of benzoyl chloride have been correlated in this manner.[5] In Eqn. (1), k and k_0 are the specific rates of solvolysis of a substrate in a given solvent and in the standard solvent (80% ethanol), respectively, m is the sensitivity to changes in solvent ionizing power (Y) and c is a constant (residual) term.

For treatment in terms of an extended form of Eqn. (1), in which an lN term is added:

$$\log(k/k_0)_{RX} = lN_T + mY_X + c \qquad (2)$$

where l is the sensitivity to changes in solvent nucleophilicity N, it is desirable to restrict all solvent nucleophilicity influences to the lN term and ionizing power scales based on the solvolyses of 1- or 2-adamantyl derivatives are recommended. Further, it is advantageous to develop Y_X scales for each X leaving group.[6]

Using initially neutral substrates, with an anionic leaving group, it is possible to develop N scales only if the m value required for the two-term equation is known. This is a major problem and scales developed initially (principally the N_{OTs} scale based on methyl *p*-toluenesulfonate solvolysis[7]) required an approximate estimate of this m value. Alternatively, a substrate with positive charge on the leaving group atom attached to the reaction center involves a neutral leaving group with a very low influence on its leaving group ability from solvent changes.[8] Indeed, to a very good approximation, with bimolecular nucleophilic attack by the solvent, the leaving group influences can be ignored and the need for a rather crude estimation avoided. The scale which is presently almost universally accepted as the solvent

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nucleophilicity scale, the N_T scale, is based on the solvolyses, over a wide variety of solvents, of the *S*-methyldibenzothiophenium ion.[4,9,10] In turn, this now allows a direct determination of the *m* value relevant to the solvolyses of methyl *p*-toluenesulfonate, which is found to be 0.55, rather than the initial rough estimate of 0.3. A secondary scale, calculated using this 0.55 value, can be designated as N'_{OTs} and is in excellent agreement with the primary N_T scale.[4]

It has been known since very early studies of the application of the Grunwald–Winstein equation that solvolyses of substrates with aromatic rings attached to a reaction center developing appreciable positive charge at the transition state tend to give dispersion in Grunwald–Winstein plots.[11] This dispersion can be treated by a similarity model approach, with development of Y_{BnX} scales[12] for each leaving group X and Y_{xBnX} scales for *x* aromatic rings entering into conjugation,[13] with the need to establish rigorously in each case that the scale does not contain an appreciable contribution from nucleophilic solvation of the developing carbocation. Alternatively, one can add an additional term to the linear free energy relationship in order to incorporate this effect. The second approach is based on the philosophy that, while the correlations cannot be expected to be as good as those using a closely related similarity model, the sensitivities obtained can be directly compared with those for other systems,[14] plus if one already has the required Y_X scale, one can use these values in conjunction with corresponding values of the universal parameter *I* to include in the correlation the influence of α-aromatic rings. We have developed an *I* scale of this type from a comparison of the solvolyses, in a wide range of solvents, of the *p*-methoxybenzyldimethylsulfonium ion and the 1-adamantyldimethylsulfonium ion.[15] These values are then incorporated as shown in the equation

$$\log(k/k_0)_{RX} = lN_T + mY_X + hI + c \qquad (3)$$

where *h* is the sensitivity of the specific rates of solvolysis of RX to changes in the value of the aromatic ring parameter *I*. Since the significance of the *hI* term is related to the development of positive charge at the reaction center, a reduction of the positive charge by nucleophilic intervention by the solvent (by either direct attack or solvation) will reduce its importance and, in many (but not all[14]) instances, the mY_X term is accompanied by only one other term, either lN_T or *hI*.

Recently, we have considered the application of the extended forms of the Grunwald–Winstein equation to solvolyses at sp^2-hybridized carbon and at heteroatoms. The solvolyses of several chloroformate and fluoroformate esters have been studied. The solvolyses can all be rationalized in terms of ionization, with varying extents of nucleophilic solvation of the developing carbocation, and association–dissociation (addition–elimination) mechanisms. When a relatively stable tertiary[16] or benzylic[17] carbocation will result, the ionization can be accompanied by expulsion of carbon dioxide. In this work, the studies at an sp^2-hybridized carbon were extended to the solvolyses of benzoyl chloride and various ring-substituted derivatives. In the ionization pathway, there is (in contrast to aryl chloroformates) the possibility of a direct stabilization of the acylium ion by the aromatic ring, which would lead to the need to incorporate an *hI* term. This effect may well be moderated, however, by improved solvation of the relatively open carbocation center and by the known involvement of oxygen lone pairs, leading to a contribution to a resonance hybrid with a carbon–oxygen triple bond and the positive charge transferred to the oxygen.[18,19]

RESULTS AND DISCUSSION

There have been many studies of the kinetics of the solvolyses of benzoyl chloride and its ring-substituted derivatives. One of the earlier studies,[20] of the solvolyses of *p*-nitrobenzoyl chloride in 60% diethyl ether–40% ethanol, led to the proposal of a duality of mechanism, with the two pathways essentially identical with those favored in this paper. However, the systems studied would proceed overwhelmingly by the bimolecular component and, also, the non-uniform kinetics observed in the early stages of each kinetic run, the basis for the duality, have never been duplicated in subsequent studies of the solvolyses of aroyl halides.

The earlier kinetic studies of solvolyses of acyl halides have been reviewed by Kivinen[21] and Talbot.[22] Both showed the incursion of an ionization reaction, proceeding through a resonance-stabilized carbocation, to be well documented. The details of the bimolecular mechanism were less well defined and Kivinen concluded that more work was needed before a detailed mechanism could be proposed.

A very comprehensive study was carried out by Hudson and co-workers and Kivinen lists 26 publications from this research group. The difficulty in distinguishing between concerted (S_N2) and addition–elimination (association–dissociation) bimolecular mechanisms was recognized and a very early proposal of what is now termed an enforced concerted mechanism as a possible cause of the difficulty was made.[23] Hudson and Moss[24] proposed that the variation of *m* with solvent composition for solvolyses in aqueous acetone or aqueous dioxane reflected a change in mechanism from bimolecular to unimolecular as the water content was increased. Swain and Mosely[25] showed that the solvolyses of *p*-nitrobenzoyl chloride correlated only very poorly with *Y* values, which they attributed to the operation of a bimolecular mechanism.

In more recent work, Lee *et al.*[26] studied the solvolyses of aroyl chlorides in binary solvents. Included in this study were solvolyses in 2,2,2-trifluoroethanol (TFE)–

ethanol mixtures. The use of fluoroalcohols, usually TFE or 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), has greatly extended the range of solvent types available for Grunwald–Winstein analyses. The conclusion reached was that the solvolyses were concerted S_N2 in character. However, in a subsequent publication,[27] it was suggested that the carbonyl addition mechanism operates in solvents of relatively low ionizing power.

Bentley and co-workers carried out a series of studies of the solvolyses of benzoyl chloride and derivatives. For the parent compound and several of the derivatives, a mechanism involving S_N2 character with bond breaking running ahead was proposed for highly aqueous solvents and a carbonyl addition mechanism in less aqueous solvents.[28]

Changes in the manner in which selectivity ratios in binary hydroxylic solvents varied with solvent composition were consistent with proposed variations in kinetic patterns, supporting the concept of a change in mechanism. In several instances successful rate–product analyses were carried out using bulk concentrations within an overall third-order kinetic scheme.[29] Song and Jencks[19] favored a combination of a concerted mechanism, with little or no bond breaking at the transition state, and an ionization mechanism.

Recently, Liu and Chen[30] reported a study of the solvolysis of benzoyl chloride and six ring-substituted derivatives, with analysis of the kinetics in terms of the Grunwald–Winstein equation, using Eqns (1) and (2). They confirmed the accuracy (within 5–20%) of previously reported specific rate values and added values for 100% TFE and several TFE–ethanol mixtures.[30] Despite Bentley and co-workers having given detailed instructions[31–33] as to how to initiate runs with benzoyl chlorides, which can be complicated by low solubility and/or low rate of dissolution, they were unable to extend the water content in aqueous acetone, ethanol or methanol beyond 40–50%. When coupled to an aversion to using available values from other laboratories, this led to their analyses all involving fewer than 20 solvent systems.

Because a large number of studies have been carried out previously, there is a large body of kinetic data available for specific rates of solvolysis. Indeed, in our analyses, we draw upon data from 10 previous publications[19,26,30–37] for the parent benzoyl chloride (47 solvents), the *p*-methoxy derivative (37 solvents), the *p*-methyl derivative (35 solvents), the *p*-chloro derivative (36 solvents, including one from Table 1) and the *p*-nitro derivative (35 solvents, including two from Table 1). In what could be considered as the traditional solvents for studying solvolysis, *p*-nitrobenzoyl chloride reacts predominantly by a bimolecular mechanism. Only by adding a value in 97% HFIP (Table 1) have we been able to find evidence for an upturn in specific rate, probably corresponding to incursion of a dominant ionization mechanism. In this connection, it should be pointed out that it was necessary to discard a literature value for the solvolysis of this substrate in 100% TFE. The value of 5.42×10^{-3} s^{-1} reported by Liu and Chen[30] is well over two orders of magnitude greater than a value of 9.9×10^{-6} s^{-1} reported earlier for 97% TFE.[32] Usually for ionization pathways these values are similar and, for bimolecular pathways, the 100% TFE value will be *lower*. We repeated the determination of the specific rate of solvolysis in 100% TFE (value reported in Table 1) and obtained a value 8500 times lower than the value of Liu and Chen. There does not appear to have been a typographical error, since the value used in figures[30] corresponds to the tabulated value.

Table 1. First-order rate coefficients for the solvolyses of *para*-substituted benzoyl chlorides at 25.0 °C

Substituent	Solvent	10^5k (s^{-1})[a]
p-Cl	97% HFIP[b]	321 ± 8
p-NO_2	97% HFIP[b]	0.177 ± 0.008
p-NO_2	100% TFE	0.0635 ± 0.0011

[a] With associated standard deviation.
[b] On a weight/weight basis.

The results of the correlation analysis in terms of Eqns (1) and (2) are shown in Table 2. *p*-Methoxybenzoyl chloride and *p*-nitrobenzoyl chloride represent two extremes in terms of Hammett substituent constant[30] and also in terms of correlation analysis of the influence of solvent variation upon the specific rates of solvolysis. *p*-Methoxybenzoyl chloride was considered[32] to solvolyze by an S_N2–S_N1 mechanism in most solvents, but with a change to carbonyl addition in 100–80% ethanol and 100–70% methanol. More recently, it has been proposed[30] that an ionization mechanism is operative over the full range of these solvents, including 100% ethanol and methanol and binary aqueous solvents rich in these alcohols. Values were obtained[30] from application of Eqn. (2) to specific rates in 17 solvents of 0.36 for l and 0.77 for m (with use of Y_{BnCl} values), and the correlation coefficient (R) was 0.955. In the present analysis (Table 2), specific rates in 37 solvents were analyzed in a parallel manner, with values of 0.31 for l and 0.81 for m, and with an R value of 0.9887.

The inferior correlation in the earlier analysis[30] probably results from the use of Y_{BnCl} values which assume an appreciable contribution to the linear free energy relationship due to positive charge developing adjacent to an aromatic ring. However, an analysis in terms of Eqn. (3) suggests, at best, only a minor contribution, a situation which will lead to overcompensation when Y_{BnCl} values are used. For the 35 solvents for which I values are available, application of Eqn. (3) leads to values of 0.37 ± 0.06 for l, 0.84 ± 0.03 for m, 0.30 ± 0.17 for h (with a probability that this contribution is not statistically significant of 0.081) and 0.09 for c. The standard error of the estimate is 0.21. The R value of

Table 2. Correlation of the specific rates of solvolysis, at 25.0 °C, of benzoyl chloride and *para*-substituted derivatives (p-XC_6H_4COCl) using one-term [Eqn. (1)] and two-term [Eqn. (2)] forms of the Grunwald–Winstein equation

X	*n*[a]	*l*[b]	*m*[b]	*c*[c]	*R*[d]	*F*[e]
CH_3O	37		0.72 ± 0.03	−0.04 ± 0.31	0.9744	657
	37	0.31 ± 0.05	0.81 ± 0.02	0.08 ± 0.21	0.9887	738
CH_3	35		0.61 ± 0.04	−0.04 ± 0.44	0.9340	226
	35	0.41 ± 0.06	0.73 ± 0.03	0.15 ± 0.29	0.9730	285
	33		0.67 ± 0.04	−0.17 ± 0.39	0.9479	275
	33	0.39 ± 0.05	0.77 ± 0.03	0.03 ± 0.21	0.9853	500
H	47		0.49 ± 0.04	−0.21 ± 0.56	0.8741	149
	47	0.51 ± 0.06	0.65 ± 0.03	0.03 ± 0.34	0.9572	246
	32		0.70 ± 0.06	−0.94 ± 0.51	0.8997	127
	32	0.47 ± 0.03	0.79 ± 0.02	−0.49 ± 0.17	0.9895	680
	12		0.32 ± 0.10 (0.010)[f]	−0.02 ± 0.39	0.7109	10
	12	1.27 ± 0.29 (0.002)[f]	0.46 ± 0.07	0.18 ± 0.23	0.9173	24
Cl	36		0.23 ± 0.05	−0.27 ± 0.61	0.5839	18
	36	0.56 ± 0.07	0.45 ± 0.04	−0.11 ± 0.36	0.8794	56
	20		0.40 ± 0.15	−0.84 ± 0.70	0.5306	7
	20	0.56 ± 0.05	0.66 ± 0.06	−0.80 ± 0.26	0.9528	84
	15		0.17 ± 0.11 (0.153)[f]	−0.25 ± 0.46	0.3880	2.3
	15	1.88 ± 0.28	0.59 ± 0.08	0.19 ± 0.22	0.9047	27
NO_2	35		−0.04 ± 0.13 (0.738)[f]	−0.76 ± 1.58	0.0587	0.1
	35	1.58 ± 0.08	0.52 ± 0.05	0.00 ± 0.46	0.9588	182
	34		0.06 ± 0.13 (0.627)[f]	−0.78 ± 1.47	0.0865	0.2
	34	1.78 ± 0.08	0.54 ± 0.04	0.11 ± 0.37	0.9689	237

[a] Number of solvents (data from Refs 19, 26, 30–37 and Table 1); the total range of solvents and the details of its division into two subgroups is presented in the Experimental section.

[b] With associated standard error.

[c] Accompanied by the standard error of the estimate.

[d] Correlation coefficient.

[e] *F*-test value.

[f] Values in parentheses are the probabilities that the associated value leads to a contribution to the overall analysis that is statistically insignificant, reported if greater than 0.001.

0.9892 is only marginally better than the value obtained for 37 solvents using Eqn. (2), and the *F*-test value falls to 444 from 738. The *l* and *m* values are very typical values for a mechanism involving ionization with a moderate nucleophilic solvation of the developing carbocation.[4]

The specific rate data for *p*-methoxybenzoyl chloride can be used to construct linear free energy correlations against the corresponding data for solvolyses of benzoyl chloride and the *p*-methyl and *p*-chloro derivatives.[36] The approximately linear portion, with a slope close to unity, can be taken as the region in which a similar ionization mechanism operates. The solvolyses with a dominant superimposed bimolecular mechanism will show appreciable positive deviations from the correlation line.

For *p*-methylbenzoyl chloride solvolyses, this treatment indicated that only the data points for 100% ethanol and 100% methanol showed appreciable deviations. For the remaining 33 solvents an excellent correlation was obtained using Eqn. (2) (Fig. 1), with a multiple correlation coefficient of 0.9853. The analysis by Liu and Chen,[30] again for 17 solvents, includes these two solvents and continues to use Y_{BnCl} values, which will be even less appropriate for the solvolyses of this substrate. Their *l* and *m* values are similar to those obtained in the present analysis, but a considerably inferior correlation coefficient (0.923) is obtained.

For the parent (unsubstituted) compound, specific rates are available in 47 solvents and these divide into 32 close to the correlation line, constructed as outlined above, and 12 solvents with appreciable positive deviations. Three solvents within the changeover region were omitted from both correlations. A good correlation is obtained for the 32 solvents within the ionization region, but only a rather

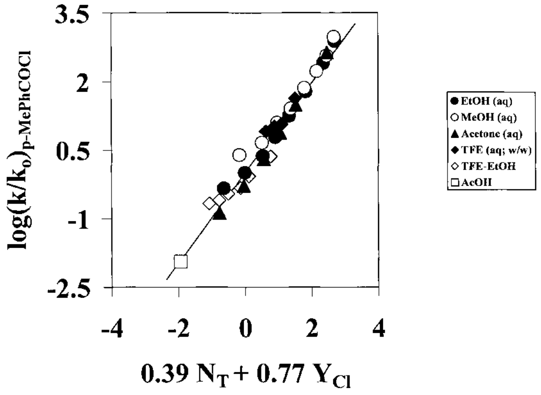

Figure 1. Plot of log (k/k_0) for solvolyses of *p*-methylbenzoyl chloride at 25.0 °C against ($0.39\ N_T + 0.77\ Y_{Cl}$). The log (k/k_0) values for 100% EtOH and 100% MeOH are not included in the correlation; they are added to show their moderate deviation from the correlation line

poor one (especially as regards the l value) for the more restricted bimolecular region. Owing to the limited range of solvent type, the l value of 1.27 ± 0.29 should be considered to be only approximately established. With a maximum of only 19 solvents available owing to the restrictions imposed by the authors, Liu and Chen attempted correlations for the solvolyses of this substrate only in terms of Eqn. (1). Presumably, with a change in mechanism, 19 solvents are not sufficient to determine the appropriate sensitivities for each of the two branches. A similar situation presumably also applied to the *p*-chlorobenzoyl chloride solvolyses, where again only a one-term correlation was attempted.

We find that the 36 solvolyses of *p*-chlorobenzoyl chloride exhibit specific rates which again can be divided into two classes, with 20 following the ionization pathway and 15 the bimolecular pathway, with only one clearly within the changeover region. The range of solvents following the bimolecular pathway is, as one would predict, greater than for the parent compound and a reasonably precise l value of 1.88 ± 0.28 can be obtained using Eqn. (2) (Fig. 2). The l value for the ionization pathway of 0.56 ± 0.05 (Fig. 3) represents a continuation of the steady increase in this value as one progresses from the *p*-methoxy to the *p*-methyl derivative and then further to the parent compound and the *p*-chloro derivative. As is to be expected for an ionization pathway, the increases in l value are accompanied by decreases in m value (corresponding to earlier transition states), with the value of 0.81 ± 0.02 for the *p*-methoxy derivative falling to 0.66 ± 0.06 for the *p*-chloro derivative.

We find that the solvolyses of *p*-nitrobenzoyl chloride show the characteristics of a bimolecular addition–elimination mechanism ($l = 1.78 \pm 0.08$, $m = 0.54 \pm 0.04$; $R = 0.9689$) for 34 of the 35 solvolyses (Table 2 and Fig. 4). Only for 97% HFIP, the solvent of lowest nucleophilicity and highest ionizing power, is there evidence for a change in mechanism, presumably to an ionization pathway. The l and m values observed are essentially identical with those for phenyl chloroformate ($l = 1.68 \pm 0.10$, $m = 0.57 \pm 0.06$), where there is independent evidence for an addition–elimination (association–dissociation) pathway with the addition step being rate determining.[38] The *p*-nitrobenzoyl chloride data were used in a linear free energy relationship plot against the specific rates of solvolysis of *p*-chlorobenzoyl chloride, and it was confirmed that the 15 previously assigned to the bimolecular pathway are now the ones lying on the plot, with the data points assigned to the ionization pathway lying above the plot. Despite the fact that their analyses using the one-term equation [Eqn. (1)] showed the equation not to apply, as was also found in the present study, Liu and Chen did not attempt an analysis of the solvolyses of *p*-nitrobenzoyl chloride in terms of Eqn. (2). They postulated an S_N2 mechanism for most solvents, but with a change to an addition–elimination route in trifluoroethanol–ethanol mixtures. This interpretation, proposing a change in the dominant bimolecular mechanism, was undoubtedly influenced by the enormous error in the specific rate value reported[30] for

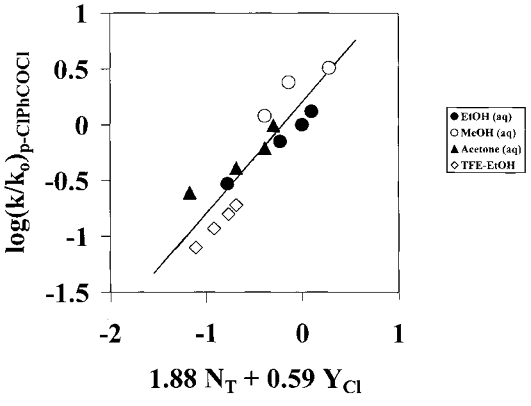

Figure 2. Plot of log (k/k_0) for solvolyses of *p*-chlorobenzoyl chloride at 25.0 °C against ($1.88\ N_T + 0.59\ Y_{Cl}$)

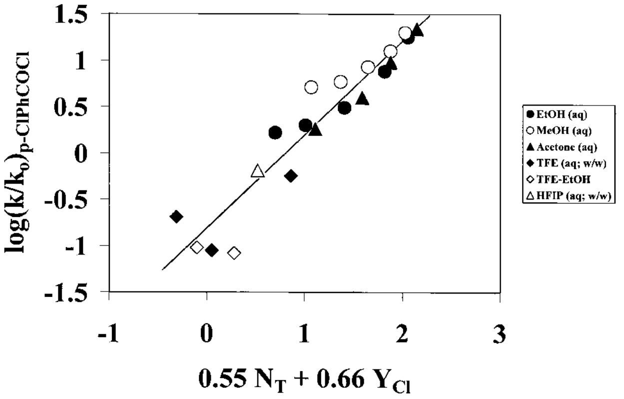

Figure 3. Plot of log (k/k_0) for solvolyses of *p*-chlorobenzoyl chloride at 25.0 °C against ($0.55\ N_T + 0.66\ Y_{Cl}$)

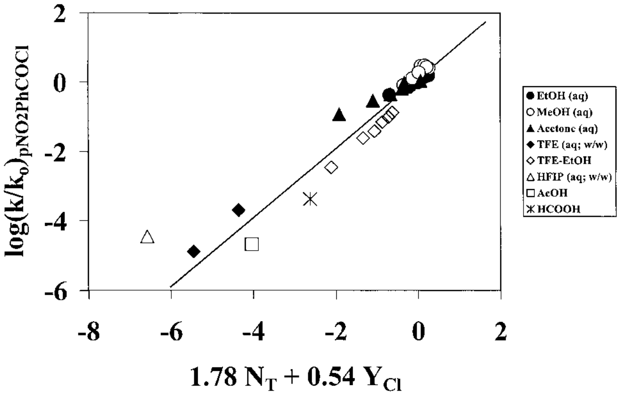

Figure 4. Plot of log (k/k_0) for solvolyses of *p*-nitrobenzoyl chloride at 25.0 °C against ($1.78\ N_T + 0.54\ Y_{Cl}$). The log (k/k_0) value for 97% HFIP is not included in the correlation; it is added to show its large deviation from the correlation line

Table 3. Correlation of the specific rates of solvolysis, at 25.0 °C, of 2,6-dimethylbenzoyl chloride in 16 solvents using various forms of the Grunwald–Winstein equation[a]

l[b]	m[b]	h[b]	c[c]	R[d]	F[e]
	0.79 ± 0.06		0.10 ± 0.32	0.9565	151
0.41 ± 0.29 (0.173)[f]	0.85 ± 0.08		0.21 ± 0.31	0.9626	82
	0.84 ± 0.04	0.95 ± 0.17	0.06 ± 0.18	0.9874	254
0.34 ± 0.15 (0.040)[f]	0.89 ± 0.04	0.92 ± 0.15	0.15 ± 0.16	0.9913	227

[a] The detailed form of the equation used for each entry can be deduced from the quoted sensitivities.
[b] With associated standard error.
[c] Accompanied by the standard error of the estimate.
[d] Correlation coefficient.
[e] F-test value.
[f] Values in parentheses are the probabilities that the associated value leads to a contribution to the overall analysis that is statistically insignificant, reported if greater than 0.001.

100% TFE, which influenced not only the interpretation of the Grunwald–Winstein plots but also the interpretation of the Hammett-type correlation of substituent effects in TFE as solvent.

We have mentioned previously how Bentley and coworkers found that trends in the variation of selectivity values[33,36] were consistent with kinetic indications of a change in mechanism.[28] In the present study, we found a similar correspondence with the changeover of mechanism from ionization to addition–elimination suggested by the kinetic analyses in terms of Eqn. (2). When the selectivity ratio (S) is defined in terms of second-order rate coefficients for production of ester relative to those for production of acid, the S values obtained in ethanol–water mixtures[33] are essentially constant for *p*-methoxybenzoyl chloride solvolyses, where an ionization mechanism over the full range of solvents is proposed from analysis of the kinetics. A maximum S value is observed in the 90–95% ethanol range for *p*-methylbenzoyl chloride[36] and for these solvolyses, the kinetic analysis indicates a change in the dominant mechanism at a very low water content within the aqueous ethanol. For the parent compound, the S values show a maximum at about 80% ethanol[36] and the kinetic analysis indicates the changeover region to be at about 60% ethanol. For the *p*-chloro derivative,[36] the corresponding values are 50% ethanol and within the 50–60% ethanol range, respectively. For the *p*-nitro derivative, the S values rise steadily as the proportion of water is increased, with no maximum value for alcohol content greater than 40% ethanol.[36,39] This is consistent with the unity of mechanism (addition–elimination) suggested by the present kinetic analysis using Eqn. (2). Beyond 40% ethanol, there is evidence for a small downturn in value, but it was recognized that the observations could also be rationalized in terms of a limiting value being reached in highly aqueous ethanol–water mixtures.[39]

Bentley *et al.*[33] found an almost constant S value for solvolyses of 2,6-dimethylbenzoyl chloride in aqueous ethanol or methanol. The magnitude was very similar to that observed for *p*-methoxybenzoyl chloride and 14 specific rates of solvolysis at 25 °C, obtained by extrapolation of data at lower temperatures, showed a good linear free energy relationship with the corresponding data for *p*-methoxybenzoyl chloride solvolysis. Liu and Chen[30] added two data points for TFE-ethanol mixtures and indicated that the ionization mechanism has less nucleophilic solvent assistance than that for *p*-methoxybenzoyl chloride. This would be consistent with the steric hindrance to be expected in the presence of the two *ortho* methyl groups.

Our analysis with only 16 data points has only marginally more than the absolute minimum of 15 considered to be required (five per independent variable incorporated into the linear free energy relationship[40]) for application of Eqn. (3). As mentioned earlier, the application of Eqn. (3) to the solvolyses of *p*-methoxybenzoyl chloride leads to a small h value with a large associated standard error. However, with less nucleophilic solvation, the importance of the hI term would be expected to increase. An analysis in terms of Eqn. (2) (Table 3) leads to a very imprecise l value of 0.41 ± 0.29 (0.173 probability that the lN_T term is not statistically significant). A much improved correlation is obtained on replacing the lN_T term by the hI term, with an m value of 0.84 ± 0.04, an h value of 0.95 ± 0.17 and a correlation coefficient of 0.9874. Reintroduction of the lN_T term and use of Eqn. (3) lead to an l value of 0.34 ± 0.15, with a probability of 0.040 that the lN_T term is not statistically significant. There is a modest increase in the value of the correlation coefficient to 0.9913, and the F-test value falls slightly from 254 to 227.

Since these solvolyses show a sensitivity to changes in the aromatic ring parameter of close to unity, a typical value for one aromatic ring adjacent to a center with appreciable positive charge developed at the transition state, the Y_{BnCl} scale should be a good similarity model. Indeed, for 12 solvents, Liu and Chen found a correlation coefficient of 0.991 for a one-term [Eqn. (1)] correlation, essentially identical with the correlation coefficients of the present study, for 16 solvents and using Eqn. (2) or (3).

CONCLUSIONS

The extended Grunwald–Winstein equation [Eqn. (2)] has been successfully applied to the solvolyses, at 25.0 °C, of benzoyl chloride and four *para*-substituted derivatives. The independent variables included in the correlation were the N_T solvent nucleophilicity scale and the Y_{Cl} solvent ionizing power scale.

The *p*-methoxybenzoyl chloride was found, for all 36 solvents, to solvolyze by one dominant pathway with sensitivities [Eqn. (2)] of 0.31 for l and 0.81 for m. These are typical values for a substrate solvolyzing by an ionization pathway with assistance provided by nucleophilic solvation of the developing carbocation. At the other extreme of substituent Hammett σ value, the *p*-nitrobenzoyl chloride gave a very good correlation in 34 of the 35 studied solvolyses, with l and m values (1.78 and 0.54, respectively) which are typical for an addition–elimination mechanism with the addition step being rate determining. The excluded solvent was 97% HFIP (very low in nucleophilicity and very high in ionizing power), which had a data point above the correlation line; this solvolysis is believed to proceed predominantly by an ionization pathway.

p-Methylbenzoyl chloride gave a good correlation, with l and m values indicating an ionization pathway with nucleophilic solvation for 33 of the 35 solvents studied. The solvolyses in 100% ethanol and 100% methanol (both relatively highly nucleophilic and low in ionizing power) lay above the correlation line. Specific rates of solvolysis of the parent compound were available in 47 solvents, and they divided into two groups. The major grouping (32 solvents) had sensitivity values (Table 3) indicating an ionization mechanism. The minor grouping (12 solvents) is restricted by the positioning of the changeover in mechanism to a less than ideal range of solvent type, but an approximate l value of 1.27 ± 0.29 and a reduced m value of 0.46 suggest a change to a bimolecular mechanism. The 36 specific rate values for *p*-chlorobenzoyl chloride divide rather more evenly, with a grouping of 20 predominantly following the ionization mode and a group of 15 predominantly following the addition–elimination route.

Previously measured[33,36] selectivity values in aqueous ethanol showed essentially a constant value for the *p*-methoxy derivative and a constant trend of change in value for the *p*-nitro derivative as the solvent composition was changed. For the other three substrates, the values passed through a maximum value at a solvent composition close to that indicated by the kinetic analyses as involving a changeover in the dominant mechanism.

Specific rates of solvolysis of 2,6-dimethylbenzoyl chloride are available for 16 solvents. The correlations were considerably improved by incorporation of a term governed by the aromatic ring parameter (I). The sensitivity to changes in I value was found to be very close to unity. This is a typical value for solvolyses where one aromatic ring is attached to a center which has developed appreciable localized positive charge at the transition state.[15,41]

EXPERIMENTAL

p-Chlorobenzoyl chloride (Aldrich, 99%) and *p*-nitrobenzoyl chloride (Aldrich, 98%) were used as received. TFE and HFIP were purified and the kinetic runs were carried out as described previously.[9] The regression analyses were performed using the ABSTAT statistical package (Anderson-Bell, Arvada, CO, USA).

All specific rates of solvolysis at 25.0 °C for which both N_T and Y_{Cl} values were available were used in the correlations. The solvent ranges covered, with compositions by volume with the other component water unless otherwise stated, are given below for each substrate, together with the details of how they are divided into two subgroups which are then independently analyzed. Solvents designated T–E represent TFE–ethanol mixtures.

p-MeOC$_6$H$_4$COCl. 100–20% EtOH; 100–20% MeOH; 90–20% acetone; 30–20% CH_3CN; 100–70% TFE (by weight); 80T–20E to 40T–60E.

p-MeC$_6$H$_4$COCl. 100% EtOH and 100% MeOH (excluded from the 33 data point correlation); 90–20% EtOH; 90–20% MeOH; 80–20% acetone; 100–70% TFE (by weight); 80T–20E to 20T–80E; 100% AcOH.

C$_6$H$_5$COCl. (a) In the region with a predominantly bimolecular pathway: 100–70% EtOH; 100–80% MeOH; 90–60% acetone; 20T–80E. (b) In the region with a predominantly ionization pathway: 50–10% EtOH; 100 H_2O; 60–10% MeOH; 40–10% acetone; 30–20% CH_3CN; 30–20% dioxane; 100–50% TFE (by weight); 80T–20E to 40T–60E; 97% HFIP (by weight); 100% AcOH; 100% HCO_2H. (c) In the borderline region: 60% EtOH; 70% MeOH; 50% acetone.

p-ClC$_6$H$_4$COCl. (a) In the region with a predominantly bimolecular pathway: 100–70% EtOH; 100–80% MeOH; 80–50% acetone; 50T–50E to 20T–80E. (b) In the region with a predominantly ionization pathway: 60–20% EtOH; 60–20% MeOH; 40–10% acetone; 100–70% TFE (by weight); 80T–20E and 60T–40E; 97% HFIP (by weight). (c) In the borderline region: 70% MeOH.

p-NO$_2$C$_6$H$_4$COCl. 97% HFIP (by weight; excluded from the 34 data point correlation); 100–20% EtOH; 100% H_2O; 100–20% MeOH; 90–20% acetone; 100% TFE; 97% TFE (by weight); 80T–20E to 20T–80E; 100% AcOH; 100% HCO_2H.

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