

Sixty years of the Grunwald–Winstein equation: development and recent applications

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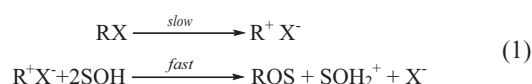
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The development of scales of values for solvent nucleophilicity and for the aromatic-ring parameter are described. These are applied to solvolytic addition to carbocations and, together with improved solvent ionising power scales, to solvolyses proceeding with a 1,2-aryl shift and to solvolytic displacements at acyl carbon and at a heteroatom, such as phosphorus or sulfur.

Keywords: Grunwald–Winstein equation, solvent nucleophilicity, solvent ionising power, aromatic-ring parameter, solvolysis

The Grunwald–Winstein equation was proposed^{1,2} in 1948 as a linear free energy relationship which was capable of correlating the influence of change of solvent upon the rate of a unimolecular solvolysis reaction (Equation (1), where SOH is a hydroxylic solvent).



The equation is as shown in Equation (2), where k is the specific rate (first-order rate coefficient) of solvolysis in a given solvent, k_0 is the specific rate of solvolysis in the standard solvent (80% ethanol was arbitrarily chosen) and m is the sensitivity to changes in solvent ionising power Y . The Y scale was originally obtained by taking *t*-butyl chloride as the standard substrate ($m = 1$). The equation can be used to predict unknown solvolysis rates, but more usually it is used to establish the magnitude of the m value, which can be taken as one indicator of mechanism.

$$\log k/k_0 = mY \quad (2)$$

The paper also reported Y values obtained with benzhydryl (diphenylmethyl) chloride as the substrate, which were recommended for use in correlations of the rates of solvolysis of α -phenylethyl chloride. This duality was a forerunner of a lively debate concerning the use of similarity models for special situations.

A major consideration, which remains an active area of research, was the influence upon the attempted correlations using Equation (2) of nucleophilic participation by the solvent.³ If covalent in nature at the α -carbon, this leads to the concerted bimolecular (S_N2) reaction. Now the nucleophilicity, as well as the ionising power, of the solvent will be an important rate-determining factor. Surprisingly, it was frequently found that over quite a large composition range of a binary solvent mixture, such as aqueous ethanol or aqueous acetone, a reasonably good linear plot was obtained for solvolyses believed to be bimolecular, but with a slope considerably reduced below unity. Indeed, the magnitude of the m values can be used as a criterion of mechanism with, for aqueous ethanol, values above 0.7 tentatively assigned to a unimolecular pathway and values below 0.5 to the bimolecular (S_N2) pathway. It is now known^{4–6} that the linear correlations of S_N2 reactions result from a collinearity between ionising power and nucleophilicity scales over fairly large composition ranges for many of the commonly studied binary solvents.

It was suggested³ that a general approach, incorporating both unimolecular and bimolecular solvolytic displacement

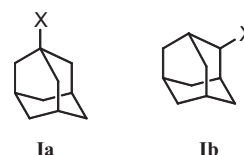
reactions, was to use a linear combination of terms, with the additional term governed by sensitivity (l) to change in solvent nucleophilicity (N), as shown in Equation (3).

$$\log (k/k_0) = lN + mY + c \quad (3)$$

It was, however, 25 years before a scale of N values became available. It is usual in more recent applications of Grunwald–Winstein equations to include a constant (residual) term (c). The advantages and disadvantages of such an addition to linear free energy relationships have been reviewed.⁷

(a) Establishment of Y_X scales

One important development involves the use of 1-adamantyl (**1a**) and 2-adamantyl (**1b**) derivatives to arrive



at scales of Y values essentially unperturbed by nucleophilic solvation and without an elimination pathway competing with substitution (Bredt's rule). For good leaving groups, **1b** is used as the substrate and for poorer leaving groups **1a**, which reacts about five orders of magnitude faster,⁸ is employed. The initial scale of Y_X values, for $X = p$ -toluenesulfonate (tosylate), was developed using 2-adamantyl tosylate as the standard substrate;⁹ values are presently available for about a dozen X groups. Details concerning the development of the scales and tables of values are presented in a review by Bentley and Llewellyn.¹⁰ Values for a nitrate leaving group¹¹ and a few additional values^{12–15} to supplement those in the review are also available. For a given solvent, Y_X values do not, normally, vary widely, but there are examples with quite large differences.^{16,17}

(b) Establishment of the N_T scale

A second development involved the establishment of several scales of solvent nucleophilicity. A major problem in applying Equation (3) to the determination of a scale of solvent nucleophilicity is that with Equation (4) it is impossible to determine directly the appropriate m_{RX} value for the solvolytic displacement reaction of the standard ($l = 1$) substrate (RX).

$$\log (k/k_0)_{RX} = N - m_{RX}Y_X \quad (4)$$

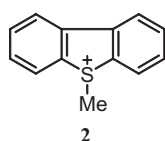
Peterson and Waller¹⁸ used relatively small concentrations of solvent molecules in liquid sulfur dioxide and arrived at relative nucleophilicities towards a standard cyclic halonium ion. The values do not, however, reproduce bulk solvent values.

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Schadt, Bentley and Schleyer^{9,19} used methyl tosylate as the standard substrate and studied the specific rates of solvolysis in a wide variety of solvents. They arrived at an estimate of 0.3 for the m_{MeOTs} value, based in part on the observation¹⁸ of equal nucleophilicities in liquid SO_2 for acetic and formic acids. Insertion of the 0.3 value into Equation (4) allowed calculation of N_{OTs} values, which gave acceptable correlations, using Equation (3), for the solvolyses of other tosylate esters. However, it can be shown²⁰ that the l values and goodness-of-fit parameters are independent of the value for m_{MeOTs} which was previously inserted into Equation (4) so as to allow the calculation of the N_{OTs} values.

Kevill and Lin⁶ minimised the mY contribution by use of the triethyloxonium ion as the standard substrate ($l = 1$), an approach suggested by the observation that the unimolecular solvolyses of the 1-adamantyldimethylsulfonium ion vary by less than one order of magnitude over a wide range of solvents²¹. The mY^+ contribution can be neglected and an N scale can be calculated using Equation (5).

$$\log(k/k_0) = N_{\text{Et}_3\text{O}^+} \quad (5)$$



The *S*-methyldibenzothiophenium ion (MeDBTh^+ , **2**) had been shown²² to have a rate of methanolysis consistent with it being a good standard substrate ($l = 1$). A wide range of N_T values was established (see ref. 23 and D.N. Kevill in ref. 24) using Equation (6). These values have become the recognised standard for considerations of solvent nucleophilicity.

$$\log(k/k_0)_{\text{MeDBTh}^+} = N_T \quad (6)$$

Applications to a wide variety of solvolytic displacements at an sp^3 -hybridised carbon have been reviewed.²⁴ The N_T scale can be used in conjunction with Y_X and/or I values as shown in Equation (7). Details of the I values are presented in Section (d).

$$\begin{aligned} \text{(a)} \quad & \log(k/k_0) = lN_T + mY_X + hI + c \\ \text{(b)} \quad & \log(k/k_0) = lN_T + mY_X + c \\ \text{(c)} \quad & \log(k/k_0) = lN_T + hI + c \end{aligned} \quad (7)$$

When N_T ²⁴ and Y_{OTs} ¹⁰ values are applied to the specific rates of solvolysis of methyl tosylate, using Equation (7b), values are obtained²⁵ of 0.96 ± 0.04 for l and 0.53 ± 0.04 for m . This gives very strong evidence that the m_{RX} value for insertion into Equation (4) should have been in the 0.50–0.55 range.^{23–25} When applied to *t*-butyl chloride solvolyses, values are obtained of 0.38 for l and 0.86 for m .^{12,24} The moderate l value is ascribed as being due to a favourable nucleophilic solvation of the developing carbocation. In strong opposition to arguments which have been presented^{26–29} against this view, mainly in terms of the differences in solvolytic behaviour relative to 1-adamantyl chloride^{12,30} ($l = 0$; $m = 1$) being electrophilic in origin rather than nucleophilic, is the observation that the *t*-butyldimethylsulfonium ion has a sensitivity to changes in solvent nucleophilicity of essentially the same value.³¹ The concept of assistance to an ionisation reaction from nucleophilic solvation of the developing carbocation is well established.^{3,32,33}

(c) Development of similarity model scales

Bentley³⁴ has recently suggested the use of *t*-butyl chloride and benzhydryl chlorides as standard substrates for consideration

of combined solvent and leaving-group effects. Several other substrates have been proposed as standards for benzylic chloride solvolyses, including α -phenylethyl chloride,^{34–36} and *p*-methoxybenzyl chloride.³⁷ Also a Y_{BnCl} scale, using initially 2-chloro-2-(3'-chlorophenyl)adamantane^{38,39} and later (to extend the range) 1-*t*-butyl-1-(4-methylphenyl)methyl chloride,⁴⁰ has been proposed.

Liu has also developed similarity model scales using standard substrates with structures related to the two used for the Y_{BnCl} scale, for correlations of benzylic bromides (Y_{BnBr}),^{15,41} *p*-nitrobenzoates⁴² and tosylates.⁴³

Consistent with the early finding that substrates with two aromatic rings at the α -carbon are not satisfactorily correlated by a similarity model scale involving only one aromatic ring in this position,^{35,36} Liu has also developed similarity model scales using substrates with the required two aromatic rings, these scales are designated as Y_{xBnX} scales. The Y_{xBnX} scales are available for several leaving groups: chloride,⁴⁴ bromide,⁴⁵ *p*-nitrobenzoate,⁴⁶ and tosylate.⁴⁷ Presumably, additional scales would be required for situations with three or more aromatic rings at the α -carbon. A review⁴⁸ includes listings of Y_{BnX} and Y_{xBnX} values. A review commentary⁴⁹ suggested that the negligible to moderate improvements upon using these specialised scales, in places of a Y_X scale, does not justify the considerable effort involved in developing them.

(d) Development of the aromatic ring parameter (I)

A major argument against the similarity model approach is that the proliferation of ionising power scales introduces a complexity which will discourage the application of the Grunwald–Winstein equation in studies of solvolytic reaction mechanism. As an alternative to the use of these scales, one can employ the already established Y_X scales¹⁰ and add the hI term (Equation (7)), where h is the sensitivity to variation of value of the aromatic ring parameter (I). The I scale (Equation 8) was established⁵⁰ from the difference in behaviour

$$I = \log(k/k_0)_{p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{SMe}_2^+} - 1.3 \log(k/k_0)_{1\text{-AdSMe}_2^+} \quad (8)$$

between the solvolyses of the (*p*-methoxybenzyl)dimethylsulfonium ion and the 1-adamantyldimethylsulfonium ion.²¹ The term can be incorporated when there are aryl groups at the α -carbon or at the β -carbon with a 1,2-aryl shift to the α -carbon (neighbouring group assistance⁵¹).

The requirement for a good similarity model is not similarity in structure but similarity in the h/m ratio for the solvolyses under consideration and the solvolyses of the chosen similarity model substrate. Sometimes, a superficially ideal substrate will have an inappropriate h/m ratio. For example, with an h/m ratio of 1.8, the standard substrate initially used to establish the Y_{BnCl} scale³⁸ usually leads to an overcorrection, relative to Y_{Cl} , when the scale is applied to the solvolyses of other monoaryl benzylic chlorides, where the h/m ratio is typically about unity.⁵⁰ Conversely, the Y_{BnOTs} scale is set up using the solvolysis of α -(*t*-butyl)benzyl tosylate,^{43,52} which does have the required h/m ratio of close to unity.⁴⁷ At present, the largest recorded⁵³ h/m ratio is 3.3, for the solvolyses of 1-(9-anthranlyl)-2,2,2-trifluoroethyl methanesulfonate.⁵⁴

(e) Applications of the aromatic ring parameter (I)

When the specific rates of solvolyses of the benzhydryldimethylsulfonium ion are correlated⁵⁵ against the $Y^{+10,21}$ and I ⁵⁰ scales, values are obtained of 0.99 ± 0.04 for h and 1.35 ± 0.10 for m , essentially the same as for the standard substrate for the I scale. It appears that introduction of a *p*-methoxy group has about the same influence on the sensitivities as when a second α -phenyl group is introduced.

Indeed, it was found that the sensitivity values increased as substituents became more electron-supplying for both (arylmethyl)methylphenylsulfonium ions⁵⁶ and arylmethyl tosylates.²⁵

Incorporation of the hI term considerably improves the correlations of the specific rates of solvolysis of a series of secondary and tertiary benzylic tosylates, *p*-nitrobenzoates, chlorides, and bromides,⁵⁷ of the parent and five monosubstituted benzhydryl bromides^{58,59} and of 2,2-dimethyl-1-(2-naphthyl)propyl bromide and 2,2-dimethyl-1-(4-methylphenyl)propyl bromide.^{58,59}

Mayr and coworkers have recently considered solvent nucleophilicity in terms of the solvent capture of carbocations generated in the solvent (see ref. 60 plus supporting information). They found that the use of extensively charge-delocalised carbocations, to avoid diffusion-controlled reaction, led to specific rates of addition which gave a good linear relationship with N_T values. This behaviour has also been observed by Kumara, Nakahara and Mishima.⁶¹

The benzhydryl cations would be expected to be formed by a process with a considerable hI contribution to the LFER and, accordingly, a negative contribution is to be expected when capture rather than release is involved. The transition state for capture will be relatively late (early for the corresponding reverse formation reaction), because of the relatively high stability of the carbocations used in the study, and this should lead to appreciable l and h values. Both Mayr and coworkers⁶³ and Bentley and Garley^{33,34} have pointed out that the cations will also be stabilised by interactions with the solvent, leading to a solvent effect on the value for the electrophilicity.⁶⁴

We now present our hitherto unpublished correlations for the capture by solvent of the three extensively studied carbocations (see ref. 60 plus supporting information). The correlation data for plots against N_T and against both N_T and l (Equation (7c)) are presented in Table 1.

The three carbocations used in the study are (4-methoxyphenyl)phenylmethyl [(*ani*)PhCH⁺], (4-methoxyphenyl)(4-methylphenyl)methyl[(*ani*)(*tol*)CH⁺] and di(4-methoxyphenyl)methyl [(*ani*)₂CH⁺]. The analyses by Mayr and coworkers (see ref. 60 plus supporting information) omitted the specific rates in methanol and ethanol and for (*ani*)PhCH⁺ also the measurement in 90% ethanol. For these values, it was believed that the measurements were near or above the upper limit of the technique being employed. We have carried out the

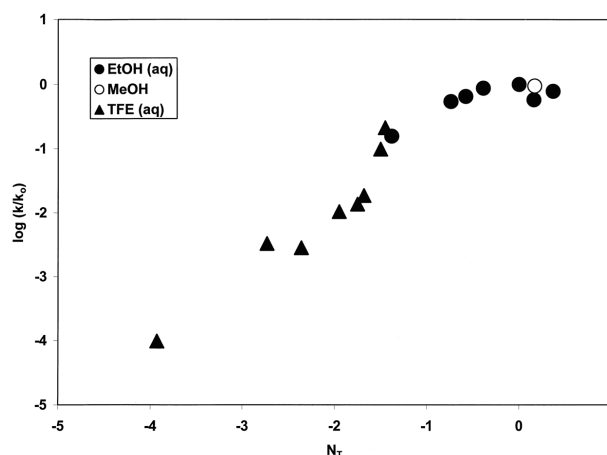


Fig. 1 Plot of $\log k$ for nucleophilic addition of solvent to the (*p*-methoxyphenyl)phenylmethyl carbocation at 20.0°C against N_T .

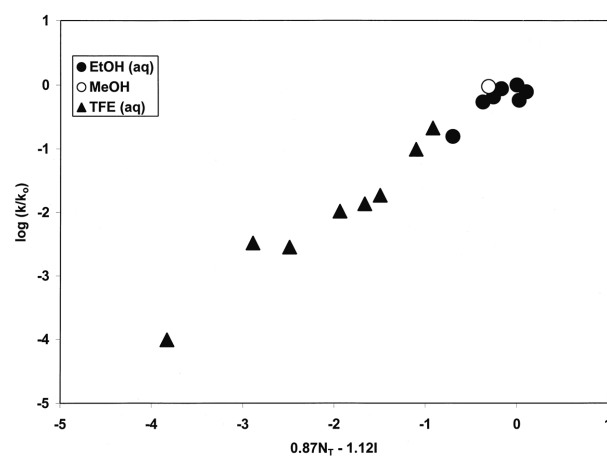


Fig. 2 Plot of $\log k$ for nucleophilic addition of solvent to the (*p*-methoxyphenyl)phenylmethyl carbocation at 20.0°C against $0.87 N_T - 1.12 l$.

correlations both with and without these data points and, except for the methanolysis point being omitted from all correlations for (*ani*)₂CH⁺, we find essentially identical multiple regression characteristics for both situations. This suggests that, with the

Table 1 Correlation^a of the specific rates of solvent capture by carbocations

Cation	E^b	n	l^c	h^c	c^c	R^d	F^e
(ani)PhCH ⁺	2.11	16	0.95 ± 0.08		0.05 ± 0.14	0.953	137
		16	0.87 ± 0.05	−1.12 ± 0.21	0.00 ± 0.08	0.986	223
		13 ^f	1.11 ± 0.08		0.39 ± 0.16	0.971	181
		13 ^f	0.91 ± 0.08	−1.07 ± 0.27	0.07 ± 0.13	0.989	218
(ani)(tol)CH ⁺	1.48	18	1.09 ± 0.07		0.17 ± 0.11	0.971	264
		18	1.04 ± 0.05	−0.83 ± 0.17	0.10 ± 0.07	0.989	332
		16 ^g	1.17 ± 0.07		0.32 ± 0.12	0.975	274
		16 ^g	1.03 ± 0.05	−0.89 ± 0.19	0.09 ± 0.09	0.991	341
(ani) ₂ CH ⁺	0.00	17 ^h	1.29 ± 0.06		0.25 ± 0.10	0.985	495
		17 ^h	1.21 ± 0.04	−0.74 ± 0.18	0.13 ± 0.07	0.994	529
		16 ^g	1.31 ± 0.06		0.29 ± 0.11	0.984	415
		16 ^g	1.18 ± 0.05	−0.85 ± 0.16	0.07 ± 0.08	0.995	598

^aUsing $\log(k/k_0) = lN_T + c$ or $\log(k/k_0) = lN_T + hI + c$, with specific rates of solvolysis from the supplementary information to ref. 60, which equation is used for a given entry can be deduced from the absence or presence of a value for h .

^bElectrophilicity parameter (ref. 64).

^cWith associated standard error.

^dMultiple correlation coefficient.

^e F -test value.

^fValues for MeOH, EtOH, and 90% EtOH omitted.

^gValues for MeOH and EtOH omitted.

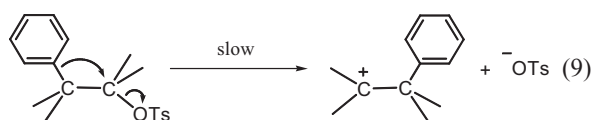
^hValue for MeOH omitted.

one exception, these data points are actually reliable and the deviations (see ref. 60 plus supporting information) result from the neglect of the I parameter influences. The N_T and I values required for the volume-volume basis studies were obtained for 2,2,2-trifluoroethanol (TFE)–H₂O mixtures by interpolation within values reported^{24,50} on a weight-weight basis. The improvements in a $\log k$ versus N_T plot upon also including the hI term, for the analyses of the solvent capture of (ani)PhCH⁺, can be seen by comparing Figs 1 and 2.

The multiple correlation coefficients are acceptable and the negative h values (–1.12 to –0.74) and appreciable l values (0.87–1.21) are as predicted. The evidence for increased sensitivity values for attack at sp²-carbon, relative to attack at sp³-carbon, has been summarised (see ref. 60 plus supporting information).

(f) *Correlation for solvolyses involving a 1,2-aryl shift*

Fujio and coworkers^{65–67} have studied the solvent effects upon the specific rates of solvolysis of several tosylate esters in which there is the possibility of appreciable anchimeric assistance accompanying a 1,2-aryl shift (Equation (9)).



Dispersion was found in the simple Grunwald–Winstein plots and a new Equation (10) was proposed. This involves a linear combination of terms governed by the ionising power scales for unassisted (Y_{OTs}) and anchimerically-assisted (Y_A) solvolysis. The Y_A scale is based on the solvolysis of *p*-methoxyneophyl[2-(*p*-methoxyphenyl)-2-methylpropyl] tosylate.^{65,68} Since charge delocalisation is involved, independent of whether the aryl group is initially at or is migrating to the α -carbon,⁶⁹ it should also be possible to correlate the specific rates with inclusion of the hI term. Indeed, we find⁷⁰ that Equation (11) gives very good to excellent correlations of the specific rates of solvolysis of several β -aryllalkyl tosylates, with h values in the 0.6–0.7 range. The correlations are about equally good with use of either Equation (10) or Equation (11), which is consistent with the observation⁷⁰ that the sensitivity values in the two correlations are related, as shown in Equation (12).

$$\log(k/k_0) = m_c Y_{OTs} + m_A Y_A \quad (10)$$

$$\log(k/k_0) = m Y_X + hI + c \quad (11)$$

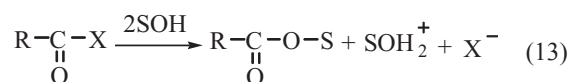
$$m = m_c + 0.52 m_A; h = 0.65 m_A \quad (12)$$

The approach of Fujio and coworkers is less versatile than the one involving introduction of the hI term but more versatile than the use of similarity models and it should be capable of dealing with multiple aromatic rings without the need to develop additional Y_A scales. However, the approach does retain one of the major drawbacks of the similarity model approach in that, for all leaving groups other than tosylate, new Y_A scales would have to be established.

The Grunwald–Winstein equation has also been applied to solvolyses involving other types of neighbouring group participation, including the solvolyses of mustard chlorohydrin and related compounds,⁷¹ glucopyranosyl derivatives⁷² and *o*-nitrobenzyl tosylate.⁷³

(g) *Application of the Grunwald–Winstein equation to solvolyses at an acyl carbon*

The Grunwald–Winstein equation has been applied to reactions of acyl chlorides and fluorides, to reactions of carbamoyl chlorides (R₂NCOCI) and to the reactions of chloroformate and fluoroformate esters. The haloformates react relatively slowly, due to resonance stabilisation of the ground state, and are conveniently followed by standard kinetic techniques (for a review of earlier studies of haloformate esters, see D.N. Kevill in ref. 74). A general equation can be expressed as in Equation (13), where a wide range of R groups includes alkyl, aryl, alkoxy, aryloxy, dialkylamino, diarylamino and alkylarylamino. In addition, for the chloroformates (ROCOCl), there have been studies of the effects on the correlations of replacing one^{75–79} or both^{78–80} oxygens by sulfur. The consequences can be dramatic with, for example, a confirmation of a proposed⁸¹ change in mechanism from bimolecular to unimolecular on substituting both of the oxygens of phenyl chloroformate by sulfur.^{77,78}



Aliphatic acyl chlorides react considerably faster but the solvolyses can be followed by rapid response conductivity measurements. An analysis on terms of Equation (7b) of the specific rates of solvolysis of acetyl chloride in 20 solvents led to values of 0.79 for l and 0.67 for m .^{82,83} Both these values are intermediate when compared to those for conventional S_N1 and S_N2 attack.

The best description is probably that the pathway is near the borderline between S_N2 attack with a loose transition state⁸² and a strong nucleophilic solvation assistance to an ionisation (S_N1) process.

Support for the nucleophilic solvation hypothesis comes from the observation that the solvolyses of carbomoyl chlorides, which are internally assisted by the lone pair of electrons on the nitrogen and are generally believed to follow an ionisation mechanism, also involve relatively high l values of 0.4 to 0.7 in their solvolyses.^{79,84,85}

The solvolyses of benzoyl chloride and its derivatives are somewhat slower than those of the aliphatic acyl chlorides and a large number of kinetic studies have been carried out. Much of these data, plus a few additional specific rates, were used in recent correlations (Equation (7b)).⁸⁶ Both ionisation and addition–elimination (association–dissociation) pathways were indicated. In the latter, the addition step is believed to be rate-determining. The two mechanisms are outlined in Equation (14). Independent evidence for two mechanisms has been obtained from a consideration⁸⁷ of selectivity values for product formation in binary hydroxylic solvents.

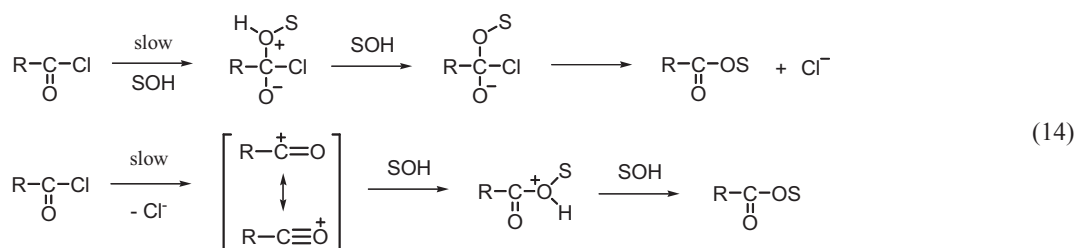


Table 2 Correlations of the specific rates of solvolysis of several chloroformate and fluoroformate esters^a

Substrate	<i>n</i> ^b	<i>l</i> ^a	<i>m</i> ^a	<i>R</i> ^c	Ref.
PhOCOCI	49 ^d	1.66 ± 0.05	0.56 ± 0.03	0.980	102
<i>p</i> -MeOC ₆ H ₄ OCOCI	44 ^d	1.60 ± 0.05	0.57 ± 0.05	0.981	102
MeOCOCI	19 ^e	1.59 ± 0.09	0.58 ± 0.05	0.977	97
EtOCOCI	28 ^f	1.56 ± 0.09	0.55 ± 0.03	0.967	96
EtOCOCI	7 ^g	0.69 ± 0.13	0.82 ± 0.16	0.946	96
<i>i</i> -PrOCOCI	20 ^h	0.28 ± 0.05	0.52 ± 0.03	0.979	98
1-AdOCOCI	15 ⁱ	~0	0.47 ± 0.03	0.985	94
OctOCOF	23 ^d	1.80 ± 0.13	0.79 ± 0.06	0.959	90
<i>i</i> -PrOCOF	20 ^d	1.59 ± 0.16	0.80 ± 0.06	0.957	93

^aUsing Equation (7b).^bNumber of solvents used in the correlation.^cMultiple correlation coefficient.^dAll solvents, no region with detectable component from ionisation mechanism.^eTwo points in highly ionising solvents omitted.^fAddition–elimination range of solvents.^gIonisation range of solvents.^hFour points in more nucleophile and less ionising solvents omittedⁱSolvolysis-decomposition mechanism with appreciable 1-AdCl formation.**Table 3** Correlations of the specific rates of solvolytic displacements at sulfur and phosphorus^a

Substrate	<i>n</i> ^b	<i>l</i> ^a	<i>m</i> ^a	<i>R</i> ^c	Ref.
<i>p</i> -MeOC ₆ H ₄ SO ₂ Cl	37	1.10 ± 0.17	0.61 ± 0.04	0.959	108
<i>p</i> -MeC ₆ H ₄ SO ₂ Cl	33	1.25 ± 0.15	0.62 ± 0.04	0.967	108
MeSO ₂ Cl	43	1.20 ± 0.05	0.52 ± 0.03	0.969	110
<i>i</i> -PrSO ₂ Cl	19	1.28 ± 0.05	0.64 ± 0.03	0.988	109
Me ₂ NSO ₂ Cl	32	1.20 ± 0.04	0.72 ± 0.03	0.985	109
(MeO) ₂ POCl	18	1.24 ± 0.14	0.45 ± 0.08	0.941	112
(MeO) ₂ PSCl	31	1.21 ± 0.10	0.60 ± 0.04	0.943	112
(Me ₂ N) ₂ POCl	27	1.14 ± 0.05	0.63 ± 0.03	0.982	113
Ph ₂ POCl	27	1.42 ± 0.10	0.54 ± 0.07	0.956	114

^aUsing Equation (7b).^bNumber of solvents used in the correlation.^cMultiple correlation coefficient.

At one extreme of the range of Hammett sigma values, *p*-methoxybenzoyl chloride solvolyses by the ionisation mechanism over the full range of solvents (*l* = 0.31; *m* = 0.81) and, at the other extreme, *p*-nitrobenzoyl chloride solvolyses by the addition–elimination pathway (*l* = 1.78; *m* = 0.54), except in solvents of very low nucleophilicity and very high ionising power. The intermediate *p*-chlorobenzoyl chloride shows a change in mechanism as one moves through the usual range of solvents (*l* = 0.56; *m* = 0.66 changing to *l* = 1.88; *m* = 0.59).

The solvolyses of benzoyl fluoride, with the considerably stronger carbon–fluorine bond, were indicated⁸⁸ to proceed by the addition–elimination pathway over the full range of solvents (*l* = 1.58; *m* = 0.82). The *Y*_{Cl} scale mimics the unavailable scale for the movement of π electrons of the carbonyl group onto the oxygen quite well, and it can be applied to the solvolyses of both acyl chlorides and acyl fluorides.

There have been quite a number of correlations of the specific rates of solvolysis of fluoroformate^{88–93} and chloroformate^{94–102} esters. Data from several of these correlations are presented in Table 2. Again, both addition–elimination and ionisation mechanisms are believed to operate. Good evidence for the addition step of the addition–elimination mechanism being rate-determining comes from the observation that, despite the stronger carbon–fluorine bond, fluoroformates frequently solvolyse faster than the corresponding chloroformate.^{89,103–105} The values (*l* = 1.66; *m* = 0.56) for phenyl chloroformate solvolyses are very robust and change little with varying subsets of data points. They can be taken as typical values for rate-determining addition to an acyl chloride. The low *m* value for solvolyses of 1-adamantyl chloroformate⁹⁴ is probably a consequence of the accompanying ejection of

CO₂ with formation of alcohol and/or ether by solvolysis and 1-adamantyl chloride by decomposition.

(h) Application of the Grunwald–Winstein equation to solvolyses at phosphorus and sulfur

Since the equations originally developed for solvolytic displacements at sp³-carbon have been shown to also apply in the presence of neighbouring-group assistance and for attack at the sp²-carbon of acyl halides, a logical further extension is to see whether they can be applied to substitutions at a heteroatom. Since several substitution reactions are known to proceed at convenient rates when taking place at phosphorus¹⁰⁶ or sulfur,¹⁰⁷ our initial correlations have been for substitutions occurring at these atoms. We have found no evidence for an ionisation pathway when acid chlorides of type RSO₂Cl,^{108–110} R₂NSO₂Cl,¹⁰⁹ (RO)₂POCl,^{111,112} (R₂N)₂POCl¹¹³ and R₂POCl¹¹⁴ are solvolysed and the specific rates correlated against *N*_T and *Y*_{Cl} using Equation (7b). As can be seen from the data presented in Table 3, very similar *l* and *m* values are observed irrespective of whether attack is at phosphorus or sulfur. Deviations of the points for TFE–ethanol mixtures are somewhat more marked than for reactions at a carbon centre.¹¹³ Our first correlations in this area, for the specific rates of solvolysis of diaryl phosphorochloridates (chlorophosphates),¹¹¹ were quite poor (*R* ~ 0.87), for reasons still not fully understood.

For the attack at sulfur, independent evidence has been presented favouring concerted (S_N2) solvolytic displacements,^{107,115} rather than the alternative addition–elimination bimolecular pathway or a unimolecular pathway. The sensitivity values obtained are consistent with such a pathway. The correlation coefficients for solvolyses at sulfur are comparable with those for solvolyses of acyl chlorides (Table 2) and those for reaction at phosphorus tend to be somewhat lower.

The general trend is consistent with the usual observation in LFER considerations of a gradual reduction in goodness-of-fit parameters as one moves away from the standard systems.

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