Full Research Paper

Consideration of the Factors Influencing the Specific Rates of Solvolysis of *p*-Methoxyphenyl Chloroformate

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Abstract: A recent correlations analysis of the specific rates of solvolysis of *p*-methoxyphenyl chloroformate (**1**) in 31 solvents using the three-term Grunwald-Winstein equation led to a sensitivity ($\underline{h}$) towards changes in the aromatic ring parameter ($\underline{I}$) of 0.85 ± 0.15. This value, suggesting an appreciable contribution from the $\underline{hI}$ term, is in contrast to the $\underline{h}$ value of 0.35 ± 0.19 that was reported for the parent phenyl chloroformate (**2**). However, for **1**, only two specific rate values were available for the important fluoroalcohol containing solvents. Values are now reported for 13 additional solvents, 12 of which have appreciable fluoroalcohol content. With all 44 solvents considered, it is found that the solvolytic behavior indicated for **1** now parallels very closely that previously reported for **2**.

Keywords: solvolysis, chloroformates, *p*-methoxyphenyl chloroformate, Grunwald-Winstein equation, aromatic ring parameter ($\underline{I}$).

1. Introduction

The Grunwald-Winstein equation (equation 1) was originally developed [1] in 1948 for the

$$\ell og\ \underline{k}/\underline{k}_0 = \underline{mY} + \underline{c} \tag{1}$$

correlation of specific rates of solvolysis of initially neutral substrates reacting by an ionization (S_N1 + E1) mechanism. In equation 1, $\underline{k}$ and $\underline{k}_o$ are the specific rates of solvolysis in a given solvent and in the standard solvent (80% ethanol), respectively, $\underline{m}$ represents the sensitivity to changes in the solvent ionizing power $\underline{Y}$ (initially set at unity for $\underline{tert}$-butyl chloride solvolyses), and $\underline{c}$ is a constant (residual) term.   It is now realized both that the scales are leaving-group dependent and that adamantyl derivatives provide better standard substrates, and a series of $\underline{Y}_X$ scales are available [2].

It was immediately realized that bimolecular (S_N2 and/or E2) reactions cannot be expected to follow such a relationship because solvent nucleophilicity ($\underline{N}$) will also be an important factor [1,3]. However, for a given type of binary solvent (such as a series of aqueous-ethanol mixtures) a linear plot based on equation 1 was frequently observed due to collinearity between the $\underline{N}$ and $\underline{Y}$ scales [4]. Such plots had $\underline{m}$ values considerable lower than unity and these values were taken as evidence for a bimolecular reaction [1,3,4].

It was further realized [3] that, in principle, the correlation could be extended (equation 2) to include

$$\ell \text{og } \underline{k}/\underline{k}_0 = \underline{\ell N} + \underline{mY} + \underline{c} \tag{2}$$

a term governed by the sensitivity $\underline{\ell}$ to changes in solvent nucleophilicity ($\underline{N}$). However, in practice, an $\underline{N}$ scale could not be developed because the appropriate $\underline{m}$ value for insertion into the equation ($\underline{\ell}$ = 1 for the standard substrate) could not be obtained. Schleyer and Bentley [5] estimated the $\underline{m}$ values at 0.3 for the solvolyses of methyl *p*-toluenesulfonate, and arrived at the $\underline{N}_{OTs}$ scale. At the present time, scales are usually based on the solvolyses of $\underline{S}$-methyldibenzothiophenium ion [6], in which the leaving group is a neutral molecule, which is little influenced by solvent change, and the $\underline{mY}$ term can be neglected. The $\underline{N}_T$ values obtained [6,7] indicated that the $\underline{m}$ for methyl *p*-toluenesulfonate is best set at 0.55 and revised $\underline{N}_{OTs}'$ values are in good agreement with $\underline{N}_T$ values [6,7].

When aromatic rings are bonded, at the transition state, to the carbon which is developing positive charge, the charge will be partially distributed into the aromatic rings. This causes changes in the solvation of the rings in going from the substrate to the activated complex [8], which in turn leads to a perturbation of analyses in terms of equation 1 or 2. This can be accommodated by use of similarity model scales in which the standard substrate contains similarly situated aromatic rings [9,10] and new ionizing power scales are devised. Alternatively, a third variable term can be added to the linear free energy relationship (equation 3), governed by the sensitivity $\underline{h}$ to changes in the aromatic ring parameter ($\underline{I}$).

$$\ell \text{og } \underline{k}/\underline{k}_0 = \underline{\ell N} + \underline{mY} + \underline{hI} + \underline{c} \tag{3}$$

The development and uses of extended forms of the Grunwald-Winstein equation was recently [11] reviewed in more detail than is presented in this manuscript.

In recent correlations [11], using the three forms of the Grunwald-Winstein equation (equations 1-3), evidence was found for a modest $\underline{hI}$ contribution in the solvolyses of $\underline{N},\underline{N}$-diphenylcarbamoyl chloride even although the aromatic rings are not directly attached to the carbon at the reaction center. This gave support to the claim by Liu [12], based on both experimental and theoretical considerations, that in these solvolyses positive charge is transferred to the aromatic rings through contributions from non-canonical resonance structures. If such an effect can be operative in the solvolyses of aromatic

carbamoyl chlorides (Ar₂NCOCl), it could also be present in the solvolyses of aromatic chloroformate esters (ArOCOCl), such as *p*-methoxyphenyl chloroformate (**1**) or phenyl chloroformate (**2**). While the h value of 0.35 ± 0.19 was essentially negligible for **2**, a much larger value of 0.85 ± 0.15 was calculated for **1** [11]. However, it was pointed out that the 31 solvents used in the analyses of the specific rates of solvolysis of **1** included only two with a fluoroalcohol component. Fluoroalcohols are extremely important, either as pure solvents or as a component of binary mixtures, in studies leading to analyses in terms of the Grunwald-Winstein equations [13-15]. Accordingly, it was suggested [11] that a more detailed investigation of the solvolyses of **1** was desirable. In this contribution we have augmented the study of the specific rates of solvolyses of **1** by adding additional solvents, with almost all of them having an appreciable fluoroalcohol component.

1   **2**
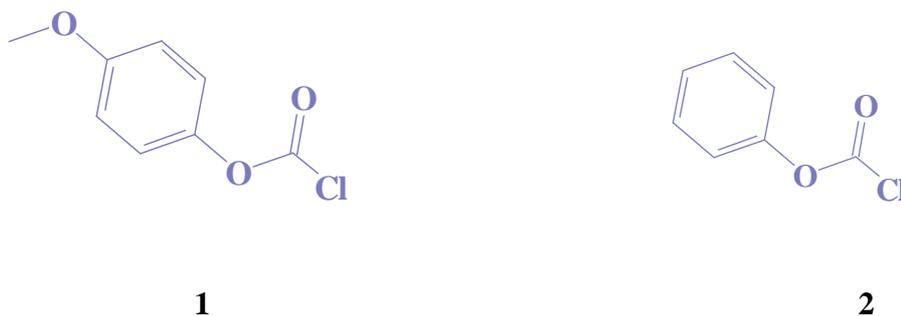
2. Results and Discussion

The solvolyses of **1** can be expressed as in Scheme 1. Values for the specific rates of solvolyses at 25.0 °C were previously available for 31 pure and binary solvents [11] and 13 additional values,

Scheme 1
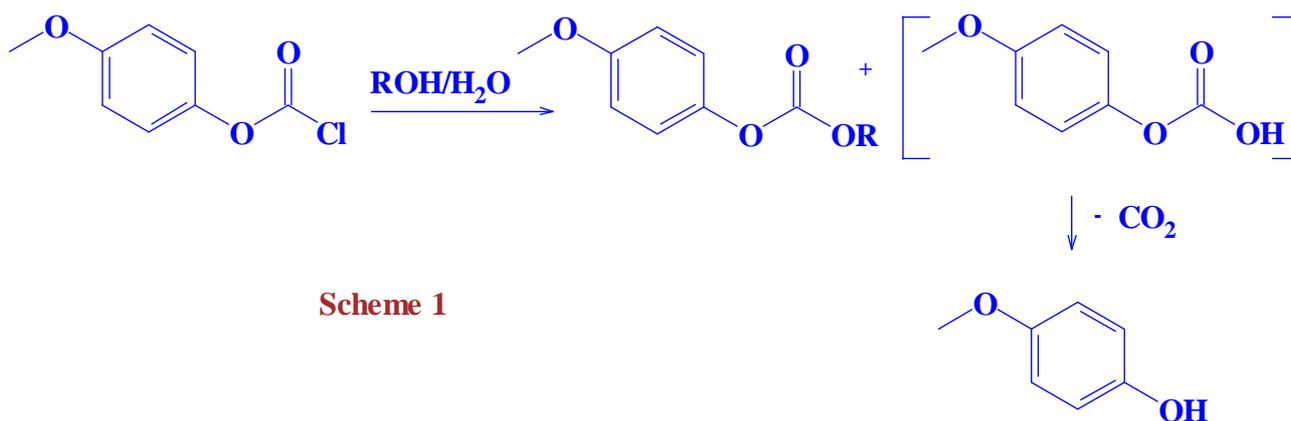
presented in Table 1, have been determined. Twelve of the new determinations are in solvents with appreciable fluoroalchohol content.

Correlations with all 44 solvents are considerably improved, primarily due to an improved variety of solvents, as regards the relationship between $\underline{N}_T$ and $\underline{Y}_{Cl}$ values, and only secondarily due to an increase in the number of data points. Of the binary mixtures with water, five involve an appreciable proportion of 2,2,2,-trifluoroethanol (TFE) and four an appreciable proportion of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). In addition, five binary compositions involve mixtures of TFE and

ethanol. Table 1 also includes the additional $\underline{N}_T$ [7], $\underline{Y}_{Cl}$ [16,17], and $\underline{I}$ [18] values needed within the correlation analysis.

Table 1. Specific rates of solvolysis ($\underline{k}$) of *p*-methoxyphenyl chloroformate in several binary solvents at 25.0 ℃ and the solvent nucleophilicity ($\underline{N}_T$), solvent ionizing power ($\underline{Y}_{Cl}$), and aromatic ring parameter ($\underline{I}$) values for the solvents.

Solvent (%)[a]	$10^5\underline{k}(s^{-1})$[b]	$\underline{N}_T$[c]	$\underline{Y}_{Cl}$[d]	$\underline{I}$[e]
90% Acetone (v/v)	15.0±0.6	-0.35	-2.22	-0.17
97% TFE (w/w)	0.0300±0.0013	-3.30	2.83	0.49
90% TFE (w/w)	0.825±0.032	-2.55	2.85	0.47
80% TFE (w/w)	8.63±0.24	-2.22	2.90	0.28
70% TFE (w/w)	15.2±0.6	-1.98	2.96	0.25
50% TFE (w/w)	52.6±2.8	-1.73	3.16	0.09
80T-20E (v/v)	3.52±0.13	-1.76	1.89	0.52
60T-40E (v/v)	17.0±0.5	-0.94	0.63	0.59
50T-50E (v/v)	32.7±1.7	-0.64	0.16	0.51
40T-60E (v/v)	59.2±2.3	-0.34	-0.48	0.43
20T-80E (v/v)	107±3	0.08	-1.42	0.31
97%HFIP (w/w)	$1.20(\pm0.13)\text{x}10^{-3}$	-5.26	5.17	0.73
70%HFIP (w/w)	7.58±0.22	-2.94	3.83	0.69

[a]Volume-volume (v/v) basis at 25.0 ℃ or weight-weight (w/w) basis, as described; other component water, except for TFE-ethanol (T-E) solvents. [b]with associated standard deviation. [c]From ref. 7. [d]From refs. 16 and 17. [e]From ref. 18.

The correlation analyses have been carried out in terms of equation 2 and 3. A major goal of the analyses is to examine the extent of the improvement (if any) in going from application of equation 2 to application of equation 3, involving the absence or presence of the $\underline{hI}$ term. The results of the correlations are presented in Table 2. For comparison, the results reported earlier [11] for the solvolyses of **1** in 31 solvents and for the solvolyses of **2** in 49 solvents are both included in the table. Also, the correlation of the specific rates of solvolysis of **2** is reported with restriction to exactly the same 44 solvents used in the correlation with **1** as the substrate.

The correlation of the specific rates of solvolysis of **1** gave a good correlation in terms of equation 2 (Figure 1), which showed virtually no improvement in the multiple correlation coefficient (0.981 to 0.982) on advancing to the application of equation 3. Further the F-test value fell appreciably (517 to 359). In particular, the $\underline{h}$ value of 0.29 ± 0.18 was much lower than the 0.85 ± 0.15 reported for 31 solvents and it was associated with a large (0.114) probability that the $\underline{hI}$ term was statistically insignificant. With the application of equation 2, the multiple correlation coefficient improves considerably (0.964 to 0.981) on inclusion of the 13 data points from Table 1. The values in Table 2 illustrate the need for a good selection of solvents for a meaningful application of extended forms of the Grunwald-Winstein equation. The observed $\underline{\ell}$ and $\underline{m}$ values are within the range previously observed for other reactions at acyl carbon which are believed to proceed by an addition-elimination

(association-dissociation) mechanism (shown for **1** in Scheme 2 below), with the addition step rate-determining [11,19,20].

Table 2. Correlations[a] of the specific rates of solvolysis of *p*-methoxyphenyl chloroformate (**1**) and a comparison with the corresponding values for phenyl chloroformate (**2**) solvolyses.

Substrate	$\underline{n}$[b]	$\underline{l}$[c]	$\underline{m}$[c]	$\underline{h}$[c]	$\underline{c}$[c]	$\underline{R}$[d]	$\underline{F}$[e]
1	44[f]	1.60±0.05	0.57±0.05		0.18±0.06	0.981	517
		1.70±0.08	0.61±0.04	0.29±0.18 (0.114)[g]	0.19±0.06	0.982	359
	31[h]	1.46±0.08	0.53±0.03		0.18±0.06	0.964	182
		1.75±0.07	0.66±0.03	0.85±0.15	0.22±0.04	0.984	274
2	49[h]	1.66±0.05	0.56±0.03		0.15±0.07	0.980	568
		1.77±0.08	0.61±0.04	0.35±0.19 (0.068)[g]	0.16±0.06	0.982	400
	44[i]	1.60±0.05	0.54±0.03		0.15±0.06	0.979	468
		1.67±0.08	0.57±0.04	0.19±0.20 (0.332)[g]	0.15±0.06	0.979	312

[a]The equation used can be deduced from the sensitivity parameters quoted. [b]Number of data points. [c]With associated standard error. [d]Correlation coefficient. [e]F-test value. [f]Specific rates are those from Table 1 plus the 31 used in ref.11. [g]Probability that the $\underline{h}\underline{I}$ term is not statistically significant, presented when greater than 0.001. [h]As reported in ref.11. [i]Using the same solvents as for the 44 data-point correlation of the specific rates of solvolysis of **1**.
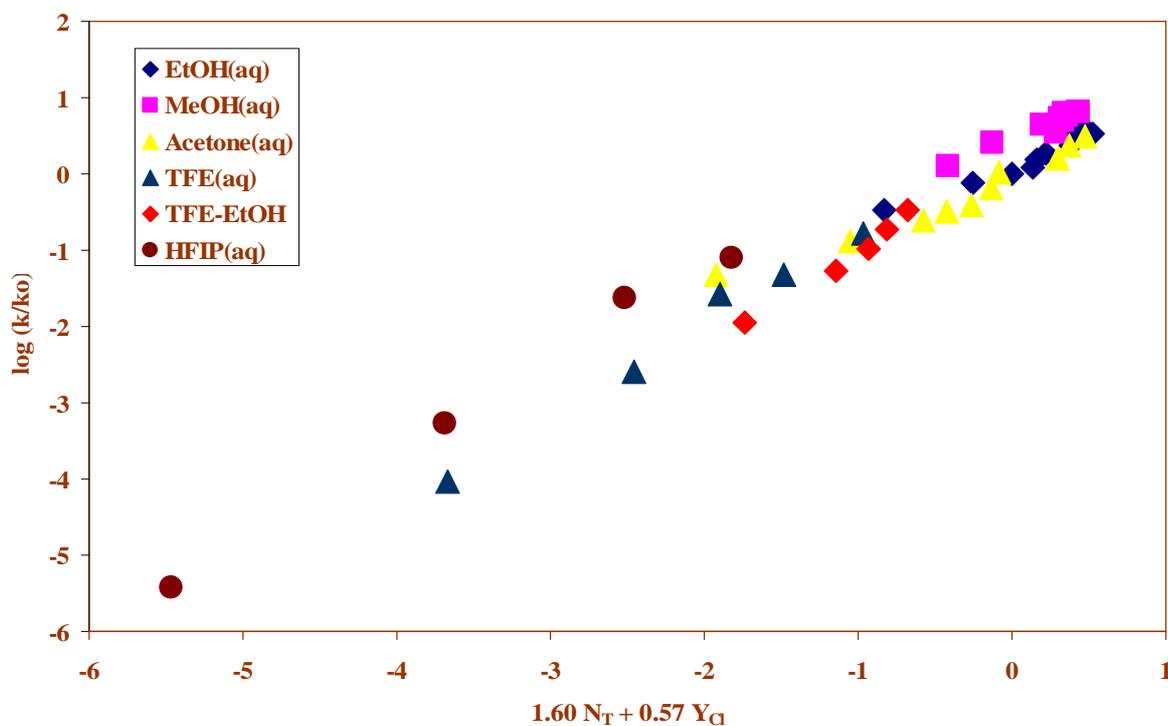
Figure 1. The plot of log ($\underline{k}/\underline{k}_o$) vs. ($1.60\ \underline{N}_T + 0.57\ \underline{Y}_{Cl}$) for the solvolyses of *p*-methoxyphenyl chloroformate (**1**) in pure and binary solvents at 25.0 ° C.

Scheme 2
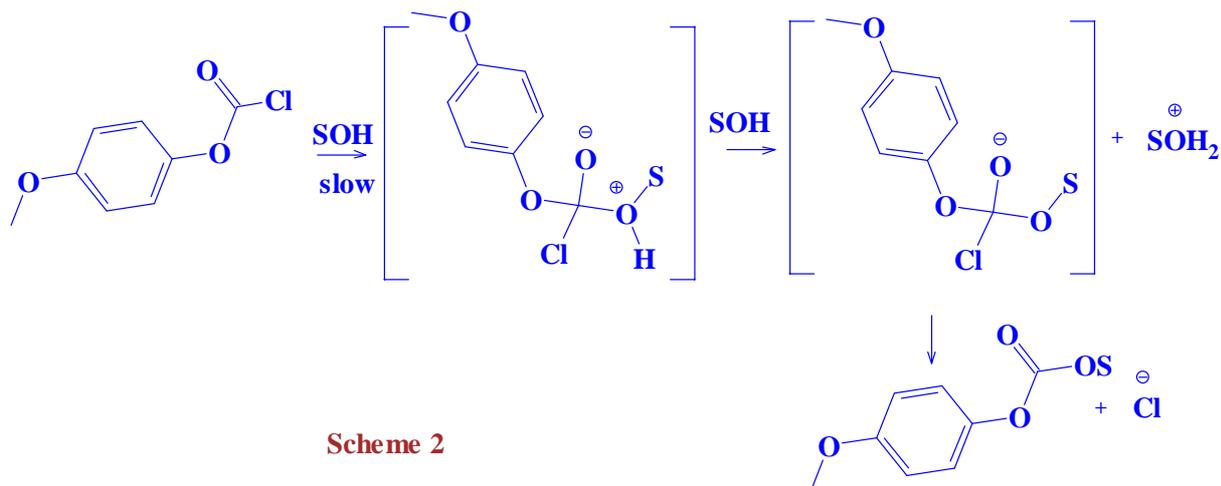
For solvolyses of **2**, the ℓ and m values change only slightly on reducing the number of solvents from 49 to 44, so as to correspond to the study with **1** as the substrate. The already lower value for h (0.35 ± 0.19) becomes slightly lower (0.19 ± 0.20) on limiting to 44 solvents. In comparing the specific rates of solvolyses of **1** and **2** in these 44 solvents, very similar correlations are observed (Table 2). This observation suggests that a very good direct linear relationship should exist between their specific rates of solvolysis. It can be seen from Figure 2 that this is indeed the case and a plot of log (k/k_o) values for **1** against those for **2** gives an excellent linear plot with a correlation coefficient of 0.998, F-test value of 9302, slope of 0.991 ± 0.010, and intercept of 0.075 ± 0.015.
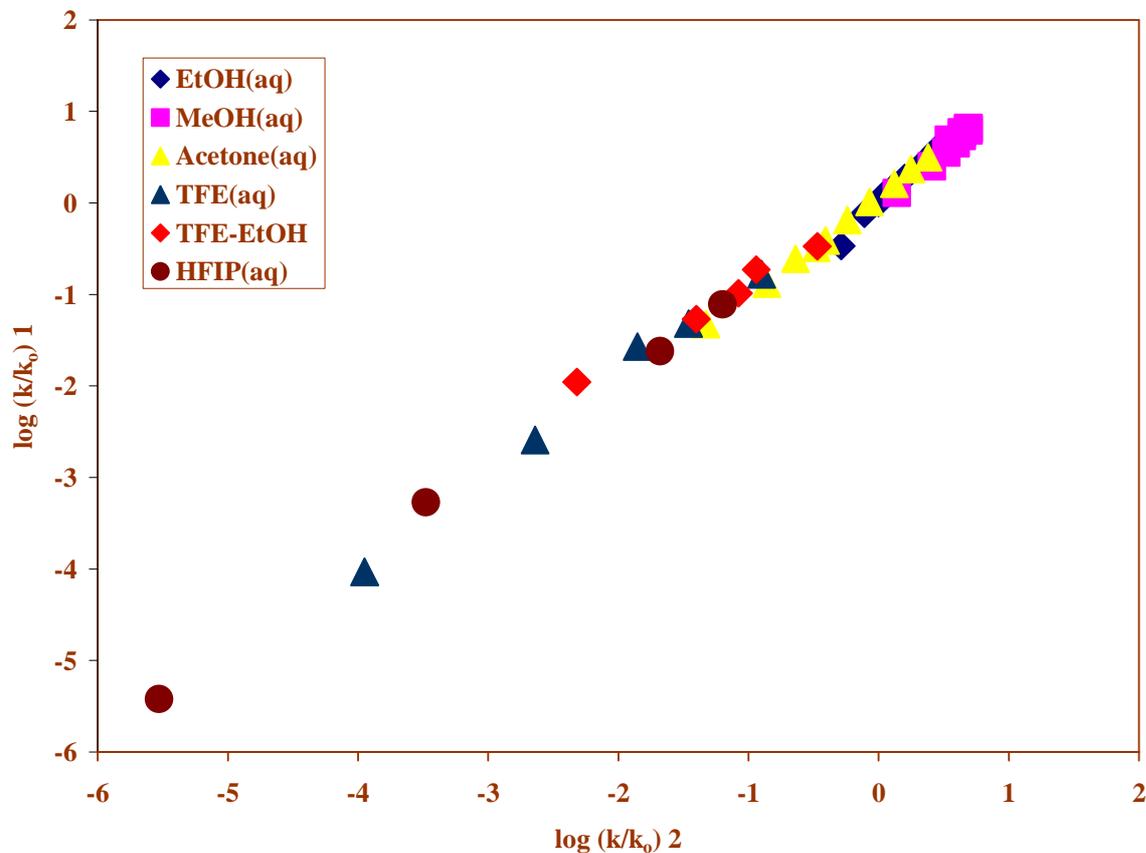
Figure 2. The plot of log (k/k_o) for *p*-methoxyphenyl chloroformate (**1**) against log (k/k_o) for phenyl chloroformate (**2**) in pure and binary solvents at 25.0 ºC.

3. Conclusions

The presently reported analyses strongly support the proposal of very similar mechanistic characteristics for the solvolyses of **1** and **2**. They demonstrate that the previous indication [11] of a meaningful hI contribution associated with the extended Grunwald-Winstein treatment of **1** but not of **2** was, as suspected at the time, an artifact, resulting from an inadequate selection of solvents being available when the specific rates of solvolysis of **1** were treated in terms of equation 3. With the addition of data for the solvolysis in several fluoroalcohol-containing solvents, the linear free energy relationship behavior becomes essentially identical to that previously observed for **2**.

4. Experimental Section

The *p*-methoxyphenyl chloroformate (Aldrich, 98%) was used as received. Solvents were purified and the kinetic runs carried out as described previously [6]. A substrate concentration of approximately 0.03 M was employed. The calculation of the specific rates of solvolysis (first-order rate coefficients) used the experimental infinity titers, at about ten half-lives, except for the runs in 97% HFIP, when portions were added to equal volumes of water and allowed to stand for 4 weeks prior to the usual titration of developed acid, and for the runs in 97% TFE, when the conventional Guggenheim treatment [21] was modified [22] so as to give the infinity titer, which was then used to calculate for each run a series of integrated rate coefficients. The specific rates and associated standard deviations, as presented in Table 1, are obtained by averaging all of the values from, at least, duplicate runs.

Acknowledgement

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