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KINETIC SOLVENT ISOTOPE EFFECT STUDIES ON THE METHANOLYSIS OF 1-PHENYLETHYL CHLORIDES

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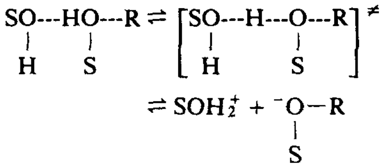
The negative slope ($\Delta\rho_Y^+ < 0$) of the Hammett-type plot using kinetic solvent isotope effect, log k_{SOH}/k_{SOD} versus σ^+, for methanolysis of 1-(Y-phenyl)ethyl chlorides is rationalized by an ion-pair mechanism in which a solvent molecule attacks the relatively stable carbocation formed in the pre-equilibrium.

INTRODUCTION

Solvolyses of 1-phenylethyl derivatives have attracted considerable attention in view of the possible involvement of an ion-pair mechanism as an alternative to the normal S_N2 mechanism.[1] Most reactions that involve the addition of water and alcohol (SOH) are subject to general base catalysis:[2]



$$\underset{H}{SO}\text{---}\underset{S}{HO}\text{---}R \rightleftharpoons \left[\underset{H}{SO}\text{---}H\text{---}\underset{S}{O}\text{---}R\right]^{\neq} \rightleftharpoons SOH_2^+ + {}^-\underset{S}{O}\text{—}R \qquad (1)$$

This type of catalysis has been observed for reactions in which carbocations (R^+) are formed or react, including the addition of weakly basic alcohols to 1-phenylethyl carbocations of moderate stability.[2,3]

Application of various mechanistic criteria to the nucleophilic substitution reactions of arenesulphonyl halides have led different investigators to propose mainly two types of mechanisms, S_N2[4] and addition–elimination (S_AN).[5] Analysis involving rate–rate profiles of solvent effects in aqueous binary mixtures on the solvolysis of 2,4,6-trimethylbenzenesulphonyl chloride indicated that S_N2 character is favoured in more polar media whereas a general base-catalysed and/or S_AN pathway is favoured in less polar media.[6]

Recently, it has been shown that the effect of ring substitution on kinetic solvent isotope effect (KSIE) values, k_{SOH}/k_{SOD}, for the solvolysis of aromatic substrates can be a promising mechanistic tool for identifying different reaction channels.[7] The plots of log KSIE vs Hammett's σ for the solvolyses of arenesulphonyl chlorides ($YC_6H_4SO_2Cl$) gave straight lines with two distinctly different slopes, 0·15 and 0·05, in methanol and water, respectively, indicating different mechanisms, general base-catalysed and/or S_AN and S_N2.[7] The slopes of such plots, $\Delta\rho_Y$ in the equation

$$\frac{\Delta \log \text{KSIE}}{\Delta\sigma_Y} = \Delta\rho_Y \qquad (2)$$

represent the change in ρ_Y due to the change in nucleophile (also solvent) from SOH to SOD. In this work, this quantity, $\Delta\rho_Y$, is used to show the involvement of an ion-pair mechanism in the solvolysis of 1-phenylethyl chlorides [$YC_6H_4CH(CH)_3Cl$] in methanol.

RESULTS AND DISCUSSION

It has been shown both theoretically and experimentally that D_2O is both a weaker base and a stronger acid than H_2O.[8] In a recent theoretical study of KSIE on the S_N2 reaction of CH_3Cl with $Cl^-(H_2O)_n$, Zhao *et al.*[9] showed that the water–water and water–chloride hydrogen bonds are stronger in D_2O rather than in H_2O. Hence a desolvation process is energetically more difficult in D_2O, resulting in a rate retardation with KSIE > 1·0, whereas, in contrast, electrophilic solvent assistance in the leaving group (LG) elimination and deuteron (proton) transfer (KSIE < 1·0) are facilitated in D_2O. This suggests that deuterated water and alcohols (SOD) are less nucleophilic but more ionizing than the corresponding non-deuterated solvents (SOH) in general.

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The magnitude of $\Delta\rho_Y$ can be related to that of ρ_{XY}, the cross-interaction constant between substituents in the nucleophile (σ_X) and substrate (σ_Y):[10]

$$\log(k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \qquad (3)$$

where

$$\rho_{XY} = \frac{\partial^2 \log k_{XY}}{\partial\sigma_X\sigma_Y} = \frac{\partial\rho_Y}{\partial\sigma_X}\left(= \frac{\Delta\rho_Y}{\Delta\sigma_X}\right) \qquad (4)$$

Since the nucleophilicity of the two solvent nucleophiles, SOH and SOD, differ very little, the hypothetical difference in the substituent σ_X values, $\Delta\sigma_X = (\sigma_X{}^H - \sigma_X{}^D)$ should be small, which in turn means that the magnitude of ρ_{XY} is large [equation (4)]. The magnitude of ρ_{XY} is known to be inversely related to the distance between the two reaction centres on the nucleophile (X) and substrate (Y), r_{XY}; a greater $|\rho_{XY}|$ therefore implies a shorter r_{XY} and hence a greater degree of bond formation. In this work, $\Delta\sigma_X$ was a constant quantity so that there will be a direct proportionality between $|\rho_{XY}|$ and $|\Delta\rho_Y|$ [equation (4)].

The $\Delta\rho_Y$ ($= \rho_{SOH} - \rho_{SOD}$) value in equation (2) is postulated to be a positive quantity [for S_N2 and addition–elimination (S_AN) reactions] or zero[7] (for S_N1 reactions). (i) If ρ_Y is positive ($\rho_Y > 0$), the reaction centre becomes more negative in the transition state (TS) and bond formation is normally ahead of bond cleavage in S_N2 reactions.[10] Since SOH is more nucleophilic than SOD, a greater degree of charge transfer is expected with SOH in the TS so that ρ_{SOH} should be greater than ρ_{SOD}, $\rho_{SOH} > \rho_{SOD}$ [this statement is actually true when ρ_{XY} ($= \partial\rho_Y/\partial\sigma_X$) < 0, since a stronger nucleophile ($\delta\sigma_X < 0$) should result in a more positive ρ_Y ($\delta\rho_Y > 0$) for $\rho_{XY} < 0$;[10] in most S_N2 reactions, ρ_{XY} is negative[10]); thus $\Delta\rho_Y > 0$.[7] (ii) If ρ_Y is negative ($\rho_Y < 0$), bond breaking is ahead of bond making in the S_N2 TS with positive charge development at the reaction centre.[10] Since bond cleavage is more facilitated in SOD, ρ_{SOD} should have a greater negative value, $|\rho_{SOD}| > |\rho_{SOH}|$, so that $\Delta\rho_Y$ is again positive.

Examples of these two cases, i.e. $\rho_Y > 0$ and $\rho_Y < 0$ with $\Delta\rho_Y > 0$, are given in Figure 1 for methanolysis of arenesulphonyl chlorides.[7] Similar plots have also been obtained for the hydrolysis of arenesulphonyl chlorides at 15 °C[11] and 25 °C.[7] The two-point lines in these figures are admittedly of low accuracy, but the trends are found to be identical in all three cases. In S_N1 reactions, the rate is independent of the nucleophile, SOH or SOD, and the KSIE of near unity (1·1–1·2)[7] (the KSIE value itself appears to have little or no clear-cut mechanistic significance,[3a] but the slope, $\Delta\rho$, for the plot of log KSIE vs σ can be used as a mechanistic tool) varies very little with substituents, indicating that $\Delta\rho_Y$ is approximately zero,[7] and hence $\rho_{XY} = 0$.[10]

The rate and KSIE for methanolysis of 1-phenylethyl chlorides are summarized in Table 1, and the plot of

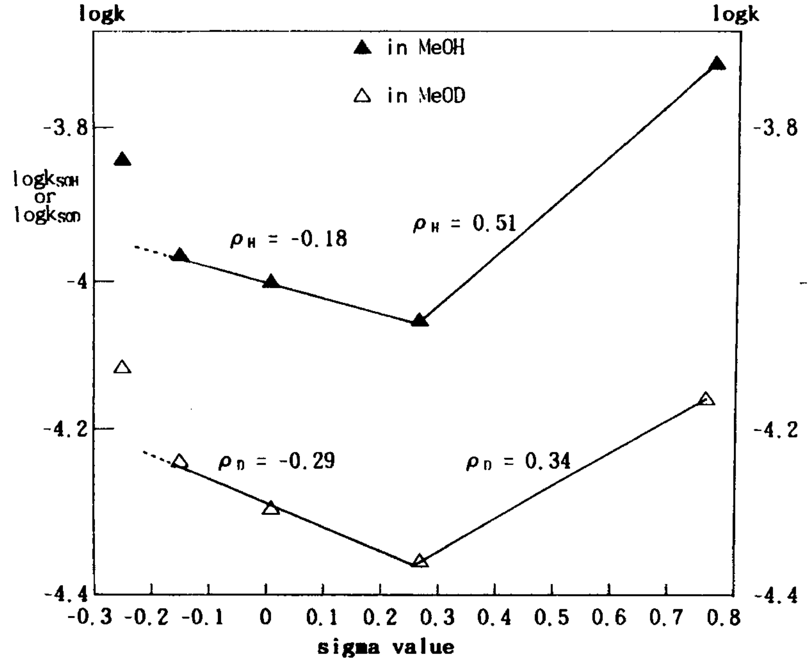


Figure 1. Hammett plot for solvolysis of *para*-substituted sulphonyl chlorides in (▲) MeOH and (△) MeOD

Table 1. First-order rate constants ($k_1 \times 10^5\ s^{-1}$) for the solvolyses of 1-phenylethyl chlorides in methanol and deuterated methanol at 65·0 °C

Y	MeOH	MeOD	k_H/K_D
p-CH_3	$892\cdot_5 \pm 2\cdot_1$[a]	$738\cdot_2 \pm 0\cdot_1$	$1\cdot20_9 \pm 0\cdot00_3$[b]
p-$C(CH_3)_3$	$624\cdot_6 \pm 3\cdot_1$	$525\cdot_1 \pm 1\cdot_9$	$1\cdot19_0 \pm 0\cdot00_7$
m-CH_3	$54\cdot5_5 \pm 0\cdot1_4$	$47\cdot9_4 \pm 0\cdot1_7$	$1\cdot13_8 \pm 0\cdot00_5$
H	$22\cdot9_5 \pm 0\cdot0_7$	$22\cdot0_7 \pm 0\cdot2_2$	$1\cdot04_0 \pm 0\cdot01_1$
p-Cl	$8\cdot28_5 \pm 0\cdot04_3$	$9\cdot06_7 \pm 0\cdot00_3$	$0\cdot91_4 \pm 0\cdot00_5$
m-Cl	$0\cdot860_9 \pm 0\cdot007_8$	$1\cdot61_9 \pm 0\cdot031_5$	$0\cdot53_2 \pm 0\cdot01_1$

[a] Standard deviation from more than three determinations.
[b] Standard error ($=1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}$.

log KSIE versus σ^+ is presented in Figure 2. The KSIE value is seen to decrease from 1·21 (Y = p-CH_3) to 0·53 (Y = m-Cl), whereas the slopes of the two straight lines in Figure 2 are both negative, $\Delta\rho_Y^+ < 0$. The negative $\Delta\rho_Y^+$ value is obviously inconsistent with any of the S_N mechanisms discussed above; since both ρ_Y^+ and $\Delta\rho_Y^+$ are negative, we expect a greater negative ρ_Y^+ value in SOH, i.e. $|\rho_{SOD}| < |\rho_{SOH}^+|$, which is opposite to the trends found in normal S_N reactions. This negative $\Delta\rho_Y^+$ value can only be rationalized by postulating an ion-pair mechanism:

$$RCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+Cl^- \xrightarrow{k_c[SOH]} \text{products} \qquad (5)$$

in which a solvent molecule attacks the carbocation, R^+, formed in a pre-equilibrium.[12,13] A highly suggestive feature for this mechanism is the common ion (Cl^-) rate depression observed with the p-$tert$-butyl derivative ($6\cdot47 \pm 0\cdot09$, $6\cdot67$ and $6\cdot84 \pm 0\cdot13 \times 10^{-3}\ s^{-1}$ with 0·01, 0·03 and 0·04 M KCl added, respectively, compared with $6\cdot84 \pm 0\cdot01 \times 10^{-3}\ s^{-1}$ with no KCl)[14] in the methanolysis at 65·0 °C. This mass law effect was absent, however, with the unsubstituted compound, for which a normal salt (ionic strength) effect with $b = 14\cdot5$ in $k_s' = k_s(1 + b[\text{salt}])$ was observed.[14] These findings are similar to those for benzhydryl and 1-adamantyl dimethylsulphonium ion solvolysis; the mass law effect was absent in the latter whereas it was observed in the former.[15]

The fact that SOH is a stronger nucleophile[8,9] is tantamount to the relationship $\sigma_X{}^H < \sigma X^D$, since a more electron-donating substituent (EDS) with a more negative σ_X leads to a stronger nucleophile. This means that

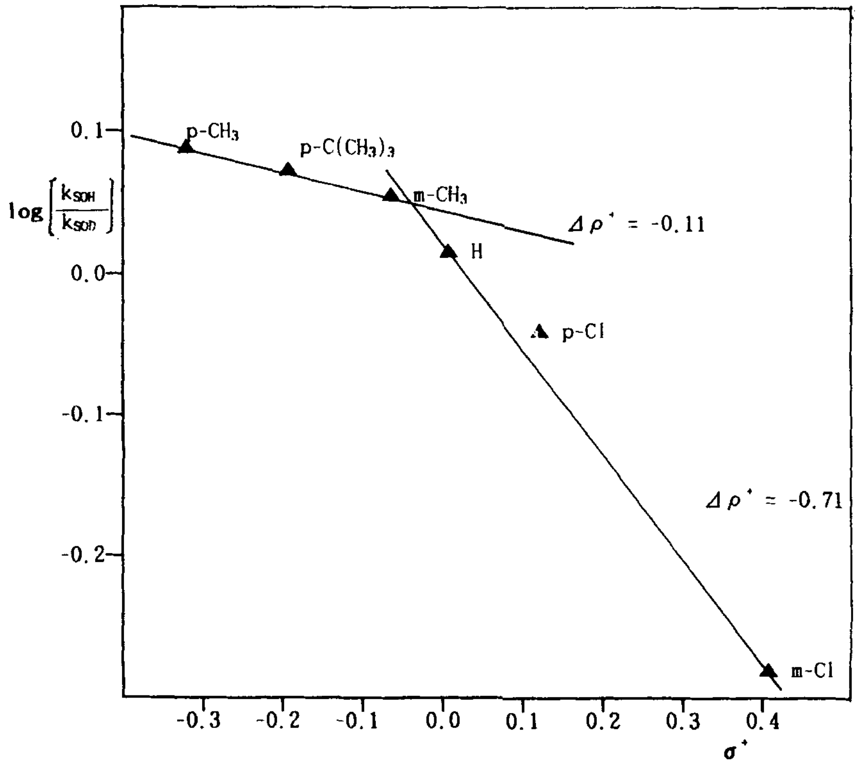


Figure 2. Hammett-type plot using kinetic solvent isotope effects, log KSIE vs σ^+, for solvolysis of 1-phenylethyl chlorides in MeOH and MeOD

ρ_{XY} values [equation (4)] for S_N2 and S_AN reactions are negative, since $\Delta\rho_Y$ is positive and $\Delta\sigma_X$ ($=\sigma_X^H - \sigma_X^D$) is negative:

$$\rho_{XY} = \frac{\Delta\rho_Y}{\Delta\sigma_X} = \frac{(+)}{(-)} < 0$$

For most of S_N reactions, the observed ρ_{XY} values were actually negative[10] (see earlier comment). If the sign of $\Delta\rho_Y$ is negative, as in this work, ρ_{XY} reverses to positive:

$$\rho_{XY} = \frac{\Delta\rho_Y}{\Delta\sigma_X} = \frac{(-)}{(-)} > 0$$

In relatively rare examples of positive ρ_{XY}, the TS was tight (with relatively large negative charge development at the reaction centre[10]), which is similar to the TS structure proposed in the nucleophilic substitution reactions of 1-phenylethyl chlorides in MeOH.[14] It is difficult, however, to compare the present results with these examples since ρ_{XY} may be a complex quantity, as discussed below for ρ_Y^+.

The ion-pair mechanism [equation (5)] has also been proposed for the solvolyses of 1-arylethyl tosylates with the *m*-Br and derivatives with more electron-withdrawing substituents in aqueous ethanol mixtures and in other highly ionizing (100 HFIP) and weakly nucleophilic (HOAc) solvents.[1a]

For this mechanism, the observed solvolysis rate constant, k_s, and the Hammett's ρ_Y^+ value are given as complex quantities;

$$\begin{aligned} \text{Rate} &= k_c[\text{SOH}][\text{R}^+\text{Cl}^-] \\ &= k_cK'[\text{RCl}][\text{SOH}] \\ &= k_cK[\text{RCl}] \qquad (6) \end{aligned}$$

where

$$K = K'[\text{SOH}] = k_1/k_{-1}[\text{SOH}]$$

Therefore,

$$k_s = k_cK \qquad (7)$$

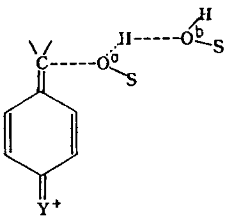
$$\rho_Y^+ = \rho_c^+ + \rho_{eq}^+ \qquad (8)$$

where ρ_c^+ is the susceptibility of charge development at C_α to the change in substituent Y as the C_α—O bond is formed, and ρ_{eq}^+ is for the pre-equilibrium ion-pair formation; ρ_{eq}^+ is known to be very large negative (−10 to −12)[1b] and ρ_c^+ is expected to be positive since transfer of negative charge from the nucleophile (SOH) to C_α will reduce the positive charge on the carbocation, R^+ ($\rho_c^+ > 0$ and $\rho_{eq}^+ \ll 0$). Since SOH is more nudeophilic than SOD, k_c will be greater in SOH, which will lead to a greater k_s in SOH than in SOD if K is also greater in SOH (see below) than in SOD or K varies little in the two solvents. This is indeed the case for electron-donating substitution (Y = EDS) in Table 1. In contrast, however, the ion pair with localized positive charge on C_α for electron-withdrawing substituents (Y = EWS) will be relatively more stabilized in SOD owing to the stronger hydrogen bonding ability to anions than in SOH, leading to a greater K, and hence a greater k_s is observed in SOD (Table 1). Considering the entire series of substrates, the ion-pair equilibrium seems to be relatively more sensitive in SOH than in SOD, i.e. $|\rho_{eq(SOH)}^+| > |\rho_{eq(SOD)}^+|$, which leads to $|\rho_{Y(SOH)}^+| > |\rho_{Y(SOD)}^+|$ despite the larger positive ρ_c^+ in SOH due to the greater nucleophilicity of SOH. The two values observed are $\rho_{Y(SOH)}^+ = -4{\cdot}38$ ($r = 0{\cdot}992$, standard deviation $s = 0{\cdot}24$, $n = 6$) and $\rho_{Y(SOD)}^+ = -3{\cdot}89$ ($r = 0{\cdot}983$, $s = 0{\cdot}24$, $n = 6$). These ρ_Y^+ values are comparable to those reported in various solvents, ranging from $-6{\cdot}3$ (100% 2,2,2-trifluoroethanol (TFE)) to $-3{\cdot}0$ (80% EtOH).[1a]

The KSIE originating from k_c will be relatively large[7] $[k_{c(SOH)}/k_{c(SOD)} \geqslant 2{\cdot}0]$ owing to general base catalysis in the addition of CH_3OH to the relatively stable cation, which is reflected in the normal KSIE observed for Y = EDS (Table 1). This effect, however, will diminish as the electron-donating power of Y decreases, since a lesser degree of base catalysis is required for the less stable cation.[3b] Moreover, a relatively greater stabilization of localized positive charge on C_α with Y = EWS in SOD should lead to an inverse equilibrium solvent isotope effect, $K_{(SOH)}/K_{(SOD)} < 1{\cdot}0$. As a result, for Y = EWS, inverse KSIEs are observed, $k_{s(SOH)}/K_{s(SOD)} < 1{\cdot}0$, which is in agreement with the results of Richard and Jencks[2] that the selectivity (in this case KSIE) of carbocations toward alcohols decreases as the carbocation becomes less stable.

Further, the localized cationic species for Y = EWS will be more sensitive to solvent ionizing power so that the difference in ρ_Y^+, i.e. $|\Delta\rho_Y^+|$, should prove to be greater with Y = EWS. Indeed the two linear parts in Figure 2 have slopes $\Delta\rho_Y = -0{\cdot}11$ ($r = 0{\cdot}998$, $s = 0{\cdot}01$, $n = 3$) and $-0{\cdot}71$ ($r = 0{\cdot}995$, $s = 0{\cdot}13$, $n = 4$) for electron-donating substituents and relatively more electron-withdrawing substituents, respectively.

Now let us elaborate on why there is a break with two distinct straight linear parts in the plots of log KSIE vs σ_Y^+ in Figure 2. Depending on the electron-donating ability of the substituent (Y) two extreme forms of cation, **I** and **II**, are conceivable.[14] In **I**, a relatively strong electron donor, Y, nearly completely delocalizes positive charge, which is stabilized by specific solvation



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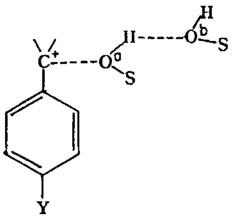

II

to the positively charged Y group, whereas in **II** an electron acceptor, Y, gives a localized positive charge on C_α with virtually no positive charge delocalization. Since the C_α atom in **I** has very little positive charge, the attacking solvent molecule, SO^aH ($S = CH_3$), requires a second molecule, SO^bH, as a general base catalyst which deprotonates partially the SO^aH in the TS; this will result in a decrease in the force constants of the $H{-}O^a$ vibrational modes, leading to a primary kinetic isotope effect (KIE), $k_H/k_D > 1{\cdot}0$.[9] This is, however, partially countered and cancelled by the concerted process of $H{-}O^b$ bond making, leading to an inverse secondary KIE, $k_H/k_D < 1{\cdot}0$. Reorganization of the delocalized structure, however, lags behind the rapid proton transfer so that the TS becomes imbalanced.[14] This means that susceptibility of C_α to the change in the electron-donating ability of Y is relatively weak so that only a small decrease in the KSIE, i.e. small negative $\Delta\rho_Y{}^+$, is observed with an increase in $\sigma_Y{}^+$. In contrast, in **II**, the relatively strong localized positive charge at C_α does not require any base catalysis by a second solvent molecule; in this case only desolvation of the hydrogen-bonded second solvent molecule (SO^bH) takes place. Both $C_\alpha{-}O$ bond-making and $H{-}O^b$ hydrogen bond-breaking processes, however, lead to an increase in the force constants of $O^a{-}H$ vibrational modes, resulting in the inverse secondary KIE observed, $k_H/k_D < 1{\cdot}0$. This effect will be enhanced as the positive charge at the C_α atom grows with the increase in $\sigma_Y{}^+$. Since there is no counteracting effect and polar effect of $\sigma_Y{}^+$ is transmitted directly to C_α without any TS imbalance, and also bond making has progressed to a substantial degree, a steep decrease in the KSIE with $\sigma_Y{}^+$ will occur and a large negative $\Delta\rho_Y{}^+$ is obtained. These interpretations are also consistent with the mechanism of aminolysis of 1-phenylethyl chlorides in methanol.[14]

In conclusion, the ion-pair mechanism is characterized by a negative $\Delta\rho_Y{}^+$ [equation (2)] in contrast to positive $\Delta\rho_Y$ values for normal nucleophilic substitution reactions.

EXPERIMENTAL

Materials. Merck analytical-reagent grade methanol and deuterated methanol were used without further purification. In the preparation of substituted 1-phenylethyl chloride,[1c,16] the corresponding acetophenone was reacted with reducing agent ($LiAlH_4$) to produce 1-phenylethyl alcohol, which was then converted into 1-phenylethyl chloride by reaction with thionyl chloride in dry chloroform at room temperature. The products were vacuum distilled and separated by column chromatography.

Kinetic products. Reaction rates were measured conductimetrically at 65·0 ± 0·05 °C in methanol and deuterated methanol. The conductivity bridge used in this work was a laboratory-made computer interface automatic A/D converter conductivity bridge and the conductivity cell was placed in a Pyrex pressure bottle with a tightly sealed cap to prevent leak of methanol vapour. Substrates were injected with a syringe. The vapour pressure inside the bottle is expected to rise with a corresponding rise in the boiling point. The rise in the external pressure (maximum *ca* 2 atm), however, is not significant enough to affect the observed rates. Pseudo-first-order rate constants, $k_1{}^{obs}$, were determined by the Guggenheim method.[17] No UV peak ($\lambda_{max} \approx 282$, 244 nm) corresponding to any alkene formed by an elimination reaction was detected.

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