# Ester Hydrolysis in Aqueous Sulphuric Acid. Effects of Solvent Ionizing Power and Nucleophilicity separated from the Effects of Protonation of Substrate†

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Rates of hydrolysis are reported for methyl, ethyl, and isopropyl toluene-*p*-sulphonates and for methyl, ethyl, isopropyl, cyclohexyl, and 2-*endo*-norbornyl methanesulphonates in 0—70% w/w aqueous sulphuric acid between 0 and 50 °C. N.m.r. studies of chemical shifts ($^1$H and $^{13}$C), showing the small extent of protonation of ethyl methanesulphonate, are also reported. The kinetic data are analysed using an equation developed from studies of solvolytic reactions in less acidic media: $\log (k/k_0)_{\mathrm{ROTs}} = lN_{\mathrm{OTs}} + mY_{\mathrm{OTs}}$, where $k/k_0$ refers to the rate of reaction in any solvent ($k$) relative to 80% ethanol/water ($k_0$), and $l$ and $m$ are empirical parameters for sensitivities of the substrate (ROTs) to solvent nucleophilicity ($N_{\mathrm{OTs}}$) and ionizing power ($Y_{\mathrm{OTs}}$) respectively. Values of $N_{\mathrm{OTs}}$ and $Y_{\mathrm{OTs}}$ are correlated with the Hammett acidity function $H_0$, and are used to calculate the relative proportions of substitution and of cyclization *via* triple bond participation in sulphonates of oct-6-yn-2-ol.

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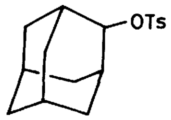
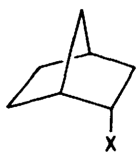
Kinetics and mechanisms of reactions in strongly acidic media (*e.g.* aqueous sulphuric acid [1a]) are usually discussed in terms of acidity functions and activity coefficients.[1] We now report a purely kinetic alternative to this thermodynamic approach. We exploit the fact that alkyl sulphonates (*e.g.* ROTs) are much less susceptible than other esters (*e.g.* carboxylates, phosphonates, and phosphates) to protonation and acid catalysis. Also a wide range of alkyl sulphonates has been studied in a variety of solvolysis reactions;[2–4] thus well understood model reactions are already available. For increasing sulphuric acid concentrations, we can examine the effects of increased solvent ionizing power and reduced solvent nucleophilicity, separated to a large extent from the effects of acid catalysis.

The range of solvents in classical studies of solvolyses of sulphonates (typically ethanol, aqueous ethanol, and acetic and formic acids[3]) has recently been extended to include weakly nucleophilic fluorinated alcohols,[2,4] and highly aqueous media.[5,6] Kinetic data for this wide range of solvents can be correlated using equation (1),[2,4] where $k$ is the rate of reaction of

$$\log(k/k_0)_{\mathrm{ROTs}} = lN_{\mathrm{OTs}} + mY_{\mathrm{OTs}} \qquad (1)$$

ROTs in any solvent relative to 80% ethanol–water and $l$ and $m$ are measures of the sensitivity of solvolyses of ROTs to solvent nucleophilicity ($N_{\mathrm{OTs}}$) and ionizing power ($Y_{\mathrm{OTs}}$), respectively. Solvent nucleophilicity ($N_{\mathrm{OTs}}$) is defined from solvolyses of methyl toluene-*p*-sulphonate (methyl tosylate, MeOTs) at 50 °C and $Y_{\mathrm{OTs}}$ is defined from solvolyses of 2-adamantyl tosylate (2-AdOTs) (**1**) at 25 °C.[2] Unfortunately 2-AdOTs and even the more soluble methanesulphonate (mesylate, OMs) are insufficiently soluble in water for kinetic studies.[5b] This technical problem can be avoided because a linear relationship has been established between logarithms of solvolysis rates for 2-AdOTs and for 2-*endo*-norbornyl tosylate‡ (2-NbOTs) (**2**; X = OTs) in a wide range of less aqueous solvents.[4–6] The corresponding mesylate (2-NbOMs) (**2**; X = OMs) behaves similarly and is sufficiently soluble in water for kinetic studies.[5f,6] Consequently it is now possible to broaden further the range of solvolytic reactions which can be examined and unified using equation (1). Here we report kinetic data for aqueous mixtures of sulphuric acid up to 70% w/w, from which we derive values for $N_{\mathrm{OTs}}$ and $Y_{\mathrm{OTs}}$.


**(1)**



**(2)**

## Results

Acquisition of reliable kinetic data in highly aqueous media is complicated by the tendency of aggregated substrates to dissolve slowly during a kinetic run.[5b] Reactions in water can be studied conductimetrically in $CO_2$-free solutions, with substrate concentrations as low as $10^{-5}$M.[5b,d,7] However, the conductimetric technique is much less reliable for highly conducting solutions (*e.g.* aqueous sulphuric acid). The usual spectrophotometric method is based on a relatively weak u.v. absorption,[8] and requires less dilute solutions (*ca.* $10^{-3}$M). Initial attempts to obtain kinetic data by this method for isopropyl tosylate gave low rate constants ($k$, 3.1—3.7 × $10^{-4}$ s$^{-1}$); more reliable independent studies are summarised in Table 1. Even for solvolyses of methyl tosylate in water at 50 °C, anomalously low (*ca.* 15%) spectrophotometric results ($k$, 1.2 × $10^{-4}$ s$^{-1}$) were sometimes obtained. Observed infinity absorbance values were often slightly higher than those predicted from the rate equation for the 10—90% reaction, on which our quoted rate constants are based. The low solubility of tosylates in aqueous media appears to be the main source of error. A linear Beer–Lambert plot ($A$ *vs.* $c$) at 240 nm for methyl tosylate up to 2.5 × $10^{-3}$M at 50 °C in 70% sulphuric acid could be obtained, but only after extensive ultrasonic treatment of solutions prepared by injecting a dilute solution (*ca.* 5%) of the tosylate in acetonitrile, dioxane or methanol. Similar results up to 1 × $10^{-3}$M at 25 °C were obtained in water. Because of these

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‡ Editorial note: strictly speaking (in IUPAC terminology) 8,9,10-trinorbornan-2-*endo*-yl tosylate.

**Table** 1. Comparison of independent studies of rates of hydrolyses of isopropyl tosylate in water at 25 °C

| $k$/s$^{-1}$ | Technique | Ref. |
|---|---|---|
| 4.106 × 10$^{-4}$ | Conductimetric | 5*d* |
| (4.13 ± 0.02) × 10$^{-4}$ | Conductimetric | 5*a* |
| (4.07 ± 0.17) × 10$^{-4}$ | Spectrophotometric | C. T. Bowen[a] |
| (4.2 ± 0.3) × 10$^{-4}$ | Spectrophotometric | Table 3 |

[a] Five measurements of rate constant in the presence of *ca.* 10$^{-3}$M-sodium acetate; see also refs. 4 and 30.

**Table** 2. Rate constants (10$^4k$/$s^{-1}$) for hydrolysis of methyl tosylate (MeOTs) and isopropyl mesylate (Pr$^i$OMs) in aqueous sulphuric acid

| [$H_2SO_4$]/M | MeOTs[a] | Pr$^i$OMs[b,c] | Pr$^i$OMs[b,d] |
|---|---|---|---|
| 0.0 | 1.35 ± 0.06 | 2.0 ± 0.4[f] | 3.6 ± 0.2[f] |
| 0.93 | 1.24 ± 0.04 | 1.9 ± 0.2 | |
| 1.82 | 1.00 ± 0.03 | 2.1 ± 0.2 | 4.2 ± 0.1 |
| 3.7 | 0.59 ± 0.02 | | 4.7 ± 0.1 |
| 5.6 | 0.30 ± 0.01 | 2.3 ± 0.3 | 5.0 ± 0.1 |
| 7.3 | 0.14 ± 0.01 | 3.1 ± 0.2 | 6.0 ± 0.8 |
| 8.1 | | 4.9 ± 0.1 | |
| 9.1 | 0.07[e] | 9 ± 1[g,h] | |

[a] Determined spectrophotometrically in duplicate at 50 ± 0.05 °C; errors shown are average deviations. [b] Determined by n.m.r. (Varian HA 100) from both appearance of product and disappearance of starting material (*ca.* 0.1M); errors shown are estimated uncertainties. [c] 25 ± 0.5 °C. [d] 30.5 ± 0.5 °C. [e] Single measurement of rate constant. [f] Reliability reduced because of large adjacent peak due to water. [g] Duplicate measurement. [h] A single spectrophotometric determination of rate constant for isopropyl tosylate in this solvent batch gave $k$ = (1.23 ± 0.05) × 10$^{-3}$ s$^{-1}$, giving a tosylate–mesylate rate ratio of 1.4:1 (slightly higher than later values; see Table 4).

**Table** 3. Rate constants (10$^4k$/s$^{-1}$) for hydrolysis of methyl, ethyl, and isopropyl tosylates in aqueous sulphuric acid[a]

| $H_2SO_4$ | | Rate constants 10$^4k$/s$^{-1}$ | | |
|---|---|---|---|---|
| % w/w[d] | [$H_2SO_4$]/M | MeOTs[b] | EtOTs[b] | Pr$^i$OTs[c] |
| 0 | 0 | 1.39 ± 0.01[e] | 1.40 ± 0.03[f] | 4.2 ± 0.3[g] |
| 10 | 1.07 | 1.26 ± 0.01 | 1.06 ± 0.04 | 4.5 ± 0.1 |
| 20 | 2.30 | 0.89 ± 0.02 | 0.93 ± 0.10[h] | 4.9 ± 0.3[i] |
| 30 | 3.70 | 0.64 ± 0.02 | 0.71 ± 0.02 | 5.2 ± 0.3[i] |
| 40 | 5.33 | 0.35 ± 0.01[j] | 0.45 ± 0.01[k] | 4.9 ± 0.3[i] |
| 50 | 6.73 | 0.177 ± 0.002 | 0.254 ± 0.013 | 6.0 ± 0.1 |
| 60 | 8.88 | 0.082 ± 0.004[l] | 0.171 ± 0.002[m] | 10.7 ± 0.1 |
| 70 | 11.15 | 0.051 ± 0.003[n] | 0.151 ± 0.007[o] | 39.2 ± 1.4 |

[a] Determined spectrophotometrically in duplicate, unless stated otherwise; errors shown are average deviations. [b] At 50 ± 0.05 °C. [c] At 25 ± 0.05 °C. [d] % w/w of A. R. grade $H_2SO_4$ (98%) in $H_2O$; up to 1% cosolvent (acetonitrile or methanol) was then added to help to dissolve the substrate. [e] Lit. (conductimetric, ref. 5*d*): $k$ = 1.38 × 10$^{-4}$ s$^{-1}$. [f] Lit. (conductimetric, ref. 5d): $k$ = 1.44 × 10$^{-4}$ s$^{-1}$. [g] See also Table 1. [h] Quadruplicate measurement of rate constant. [i] Triplicate measurement of rate constant. [j] A single kinetic run for methyl mesylate, studied by n.m.r., gave $k$ = (2.36 ± 0.05) × 10$^{-5}$; hence $k_{OTs}/k_{OMs}$ = 1.48. [k] A single kinetic run for ethyl mesylate, studied by n.m.r. gave $k$ = (2.73 ± 0.10) × 10$^{-5}$; hence $k_{OTs}/k_{OMs}$ = 1.65. [l] Duplicate kinetic runs for methyl mesylate, studied by n.m.r. (one run in a thermostatically controlled probe, the other by analysis of quenched samples), gave $k$ = (7.64 ± 0.16) × 10$^{-5}$; hence $k_{OTs}/k_{OMs}$ = 1.07. [m] A single kinetic run (n.m.r.) for ethyl mesylate gave $k$ = (1.49 ± 0.05) × 10$^{-5}$; hence $k_{OTs}/k_{OMs}$ = 1.15. [n] A tosylate–mesylate rate ratio of 0.8:1 was obtained by Fourier transform n.m.r. studies of both mesylate and tosylate in approximately 70% $D_2SO_4$–$D_2O$. [o] A single kinetic run (n.m.r.) for ethyl mesylate gave $k$ = (1.45 ± 0.04) × 10$^{-5}$; hence $k_{OTs}/k_{OMs}$ = 1.04.

experimental uncertainties we report the results of two independent spectrophotometric kinetic investigations (Tables 2 and 3), and of studies of the more readily soluble mesylates by $^1$H n.m.r. spectroscopy. Consistent tosylate : mesylate rate ratios further support the reliability of the data (Table 3, footnotes *j*—*o*, and Table 4), although experimental uncertainties are larger than those for more usual solvolyses.

Kinetic data for methyl tosylate and for isopropyl mesylate are shown in Table 2. Kinetic data for methyl, ethyl, and isopropyl tosylates are shown in Table 3, and for isopropyl, cyclohexyl and 2-*endo*-norbornyl mesylates are shown in Tables 4 and 5. Solvolyses of isopropyl mesylate were also examined by pH-stat techniques at different values of pH (see Table 6).

N.m.r. spectral data ($^1$H and $^{13}$C) for ethyl mesylate over a wide range of solvent compositions are shown in Table 7. This compound is readily soluble and unreactive under the conditions studied.

## Discussion

*Extent of Protonation of Sulphonates.*—We employed the $\alpha - \beta$[9] (or internal chemical shift[10]) comparison method to obtain estimates of the percentage of protonated substrates in the various sulphuric acid mixtures. Such studies are complicated by solvent effects on chemical shifts,[9—11] but the method is successful for $^1$H n.m.r. spectra of carboxylate esters,[9] which are structurally very similar to ethyl mesylate. Ethyl acetate shows a change in $\alpha - \beta$ of 26 Hz from 20 to 98% $H_2SO_4$,[9] to be compared with only 4 Hz for ethyl mesylate (Table 7). Ethyl mesylate is extensively protonated in superacid media, as shown by the $\alpha - \beta$ value of over 40 Hz (Table 7), but this high value may include a contribution from solvent effects; the corresponding $\alpha - \beta$ value for protonated triethyl phosphate in $FSO_3H$ at −60 °C is only 14 Hz (relative to the neat liquid ester at room temperature).[12] If we assume that protonated ethyl mesylate would have an $\alpha - \beta$ value in the range 14—48 Hz in the absence of solvent effects, we can estimate that it is protonated to the extents of 1—3% in 70% $H_2SO_4$, < 1% in 60 $H_2SO_4$, and 10—30% in 98% $H_2SO_4$.

Independent results support the lower end of our range of estimates. It appears that sulphonic acids and sulphonate esters are not extensively protonated in 98% (concentrated) $H_2SO_4$. There is one very surprising estimate that 0.4M-alkyl tosylates, even in $FSO_3H$, are only 5% protonated.[13] It has been stated (without details of supporting cryscopic and/or conductimetric experiments) that methyl mesylate is a non-electrolyte in 100% $H_2SO_4$.[14] It has also been found that (i) there is no change in the conductivity of 100% $H_2SO_4$ when methanesulphonic acid is added;[15] (ii) there is no change in the chemical shift of the methyl group of methanesulphonic acid between $H_0$ values of 9 and 13 (90% $H_2SO_4$ to 7% $SO_3$ in oleum);[16] (iii) aromatic sulphonic acids are half-ionized at $H_0$ *ca.* −6.3 (*ca.* 70% $H_2SO_4$),* but further protonation occurs at much higher values of $H_0$.[16]

Although we had initially hoped to apply $^{13}$C n.m.r. as a more sensitive measure of the extent of protonation of substrates,[18]

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* This implies that some of our spectrophotometric studies of kinetics have been applied successfully to cases where there is incompletely dissociated toluene-*p*-sulphonic acid. A Beer–Lambert plot (*A vs. c*) for toluene-*p*-sulphonic acid at 273 nm in 70% $H_2SO_4$ was close to linear only in the range 1 × 10$^{-4}$ to 1 × 10$^{-3}$M, the concentration range for our kinetic measurements. Agreement between spectrophotometric and n.m.r. kinetic measurements has been reported even for alkyl tosylates in 96% $H_2SO_4$.[17]

**Table 4.** Rate constants ($k$) for hydrolysis of isopropyl, cyclohexyl (Cyhex) and 2-*endo*-norbornyl (2-Nb) mesylates, and tosylate–mesylate rate ratios ($k_{OTs}/k_{OMs}$) in aqueous sulphuric acid[a]

| $H_2SO_4$ % w/w[b] | Rate constants $10^4k/s^{-1}$ Pr$^i$OMs | CyhexOMs | 2-NbOMs | $k_{OTs}/k_{OMs}$ |
|---|---|---|---|---|
| 0 | 2.09[c] | 3.99 ± 0.01[d,e] | 1.19 ± 0.01[d,f] | 2.1[g] |
| 10 | | 4.8 ± 0.2 | 1.63 ± 0.23 | 2.0[h] |
| 20 | 2.5 ± 0.3 | | 2.38 ± 0.05 | 1.8[i] |
| 30 | | 6.8 ± 0.6 | 2.65 ± 0.05 | 1.7[h] |
| 40 | | | 4.0 ± 0.1 | 1.6[j] |
| 50 | 3.5 ± 0.3 | 11.7 ± 0.5[k] | 6.4 ± 0.4[k] | 1.4[i] |
| 60 | 9.7 ± 1.5[l] | | 14.9 ± 0.1[m] | 1.1[i,n] |
| 70 | 32 ± 3[o] | 150[p] | 62 ± 6[q] | 1.0[i] |

[a] Determined by n.m.r. in duplicate at 25 ± 0.2 °C, except where stated otherwise. [b] Solvents are the same stock solutions as for Table 3, with the addition of 1% $D_2O$ and 0.5% [$^2H_6$]acetone. [c] Ref. 5*a*; other lit. values $10^4k/s^{-1} = 1.965$ (ref. 5*d*) and 2.01 (ref. 5*f*); our data (n.m.r.) are given in Table 2. [d] Determined conductimetrically in duplicate. [e] Lit. $k = (4.26 \pm 0.20) \times 10^{-4}\ s^{-1}$ (ref. 5*a*). [f] Lit. $k = (1.28 \pm 0.05) \times 10^{-4}$ (ref. 5*a*) and $1.33 \times 10^{-4}$ (ref. 5*f*). [g] Ref. 5*a*. [h] Interpolated. [i] Estimated from data for isopropyl sulphonates (Tables 3 and 4), assuming an approximately linear trend; see also Table 3, footnotes *n* and *o*. [j] Assumed from data for methyl and ethyl sulphonates in this solvent (Table 3, footnotes *j* and *k*). [k] Triplicate measurement of rate constant. [l] Single measurement of rate constant. [m] At 10.0 °C, $k = (2.17 \pm 0.04) \times 10^{-4}$. [n] See also Table 3, footnote *m*. [o] At 10.0 °C, $k = (4.9 \pm 0.8) \times 10^{-4}$ (triplicate measurement) and at 0.0 °C, $k = (1.2 \pm 0.1) \times 10^{-4}$. [p] Calculated from the following data at lower temperatures: at 10.0 °C, $k = (2.13 \pm 0.07) \times 10^{-3}$ and at 0.0 °C, $k = (5.13 \pm 0.25) \times 10^{-4}$. [q] At 10.0 °C, $k = (1.2 \pm 0.2) \times 10^{-3}\ s^{-1}$ (triplicate measurement) and at 0.0 °C, $k = (2.42 \pm 0.25) \times 10^{-4}\ s^{-1}$

**Table 5.** Activation parameters for hydrolyses of isopropyl, cyclohexyl (Cyhex), and 2-*endo*-norbornyl (2-Nb) mesylates[a]

| Substrate | Solvent % (w/w) $H_2SO_4$ | $\Delta H^{\ddagger}$ kcal mol$^{-1}$ | $\Delta S^{\ddagger}$ cal K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|
| Pr$^i$OMs | $H_2O$[b] | 22.1 | −1.3 |
| Pr$^i$OMs | 70% | 20.7 | −0.6 |
| CyhexOMs | $H_2O$[c] | 22.3 | 0.9 |
| CyhexOMs | 70% | 21.3 | 4.7 |
| 2-NbOMs(**2**) | $H_2O$[d] | 21.4 | 6.9 |
| 2-NbOMs(**2**) | 60% | 21.0 | −1.1 |
| 2-NbOMs(**2**) | 70% | 20.3 | −0.5 |

[a] Additional kinetic data for % $H_2SO_4$ mixtures given in footnotes to Table 4. [b] Ref. 5*d*. [c] Ref. 5*a*. [d] Ref. 5*f*.

**Table 6.** Effect of pH on rates of hydrolysis of isopropyl mesylate at 25 °C[a]

| pH | $k/s^{-1}$ |
|---|---|
| 7.0 | $(2.33 \pm 0.04) \times 10^{-4}$ |
| 3.5 | $(2.09 \pm 0.01) \times 10^{-4}$ |
| 2.2 | $(2.13 \pm 0.26) \times 10^{-4}$ |
| 1.0[b] | $(2.09 \pm 0.10) \times 10^{-4}$ |
| 3.5[c] | $(2.22 \pm 0.08) \times 10^{-4}$ |

[a] Determined in duplicate at 25.00 ± 0.01 °C by auto-titration with 0.01M-NaOH in pH-stat mode using a Radiometer RTS822 autotitration system; see Table 4 for literature values. [b] Manual titration. [c] With 0.01M-NaCl added.

**Table 7.** Differences in chemical shifts (Hz) between $CH_3$ and $CH_2$ of ethyl mesylate in aqueous sulphuric acid[a]

| Wt. % $H_2SO_4$[b] | $^1H$ N.m.r. | $^{13}C$ N.m.r. |
|---|---|---|
| 16 | 0.0[c] | 0.0[d] |
| 30[e] | 0.0 | |
| 42 | −0.2[c] | 4.4 |
| 50[e] | 0.0[d] | |
| 60[e] | −0.2 | |
| 61 | 0.2[c] | 18.4 |
| 70[e] | 0.4 | |
| 76 | 1.2[c] | 30.7 |
| 80[e] | 1.6 | |
| 90[e] | 3.3 | |
| 90 | 3.6[c] | 57.2 |
| 98[e,f] | 4.3 | |
| ($FSO_3H$)[g] | 42, 48[h] | |

[a] Estimated error limits ±0.5 Hz. [b] For acid molarities see Table 3. [c] Preliminary measurements using Perkin-Elmer R24B 60 MHz n.m.r. instrument. [d] Arbitrarily set to zero for comparison with the other data; the absolute values observed were 299.0 Hz ($^1H$) and 1 374.1 Hz ($^{13}C$). [e] With 1% $D_2O$ added to stock solutions of acid. [f] A.R. concentrated $H_2SO_4$. [g] Containing $SbF_5$ and $SO_2ClF$, ref. 2. [h] By comparison with $SO_2ClF$ (without acid) as solvent at −60 °C (ref. 21).

the reliability of the technique now appears to be questionable. There are often severe complications from medium effects,[19a] despite preliminary indications that medium effects could be ignored.[19b] It has also been reported that samples underwent considerable heating during the 1—2 h required for data collection.[20] We observed a gradual and substantial increase in frequency differences between signals for α- and β-carbon atoms for ethyl mesylate (Table 7), which we cannot relate to extent of protonation.

*Solvent Ionizing Power* (*$Y_{OTs}$*) *for Aqueous Sulphuric Acid*.—The solvent ionizing power of strong acids could be regarded as a result of the combined effects of solvent polarity and protonating power of the solvent. Such $Y$ values would be highly dependent on substrate basicity, whereas we wish to establish one $Y$ parameter for interpreting solvent effects on kinetic data for a wide range of esters (*e.g.* carboxylates and phosphonates). Consequently, we wish to minimise the kinetic effects of protonation. Sulphonates appear to be much less susceptible than other esters to protonation followed by rapid hydrolysis. There is no change in the rate of hydrolysis of isopropyl mesylate between pH 1 and 7 (Table 6). Also rates of solvolyses of methyl tosylate decrease as the % $H_2SO_4$ increases to 70% (Table 3). However, the rates do increase at higher acidities (*e.g.* in 98% $H_2SO_4$).[17] As protonation of ethyl mesylate is just detectable in 70% $H_2SO_4$ (see before), we have limited our present study to the solvent range 0—70% $H_2SO_4$. Because the protonated substrate will react faster than the unprotonated substrate,[17] it seems likely that our $Y$ values for 70% $H_2SO_4$ will include a contribution from protonation of the substrate. A much less likely mechanistic complication under our experimental conditions is alkoxy–sulphur cleavage, which is observed for protonated methyl mesylate in superacid, but *not* for protonated ethyl mesylate.[21]

New $Y_{OTs}$ values were initially obtained from the linear relationship [equation (2)] between rates of solvolyses of 2-

$$\log(k/k_0)_{2\text{-NbOTs}} = 0.69Y_{OTs} \qquad (2)$$

NbOTs and $Y_{OTs}$ in eleven typical solvolysis media (see Table 9, footnote *a*).[2,4] Rate data for 2-NbOMs (Table 4) were converted into rate data for the tosylate using the small rate ratio ($k_{OTs}/k_{OMs}$), which depends slightly on solvent but negligibly on the nature of the alkyl group.[5b] These rate ratios were calculated from solvolyses of isopropyl sulphonates, for which data for both tosylates and mesylates could be obtained (Table 4). Their reliability was confirmed by selected additional studies of

**Table 8.** Solvent ionizing power ($Y_{OTs}$) and nucleophilicity ($N_{OTs}$), activity of water ($a_{H_2O}$), and Hammett acidity function ($H_0$) for aqueous sulphuric acid

| $H_2SO_4$ % w/w | $Y_{OTs}$[a] | $N_{OTs}$[b] | log $a_{H_2O}$[c] | $H_0$[d] |
|---|---|---|---|---|
| 0 | 4.04 | −0.42 | 0 | |
| | 4.1[e,f] | −0.44[f] | | |
| 10 | 4.22 | −0.51 | −0.019 | −0.43 |
| 20 | 4.39 | −0.71 | −0.060 | −1.10 |
| 30 | 4.43 | −0.87 | −0.124 | −1.82 |
| 40 | 4.67 | −1.20 | −0.251 | −2.54 |
| 50 | 4.90 | −1.57 | −0.453 | −3.41 |
| 60 | 5.29 | −2.02 | −0.788 | −4.51 |
| 70 | 6.1[g] | −2.5[g] | −1.352 | −5.92 |

[a] From simultaneous equations (3) and (4) [$k_0 = 3.2 \times 10^{-7}$ (ref. 4) and $2.22 \times 10^{-5}$ (ref. 2)]; kinetic data from Tables 3 and 4. [b] From equation (4). [c] Data from ref. 1*a* (p. 15). [d] Data from ref. 1*a* (p. 37), first reported in ref. 23*a*; slightly more negative values (0.04—0.14 more negative) are reported in ref. 23*b*. [e] Based on kinetic data for 2-adamantyl mesylate (ref. 5*a*). [f] Ref. 5*b*. [g] This value probably includes significant contributions from solvolysis of protonated substrate.

solvolyses of methyl and ethyl sulphonates (Table 3, footnotes *j*—*o*). Whilst the $Y_{OTs}$ values derived were satisfactory, slightly better agreement with the published $Y_{OTs}$ values for pure water was obtained from equation (3), which allows a small $lN$ term

$$\log(k/k_0)_{2\text{-NbOTs}} = 0.05N_{OTs} + 0.72Y_{OTs} \qquad (3)$$

[equation (1)] for the solvolyses of 2-*endo*-norbornyl tosylates (for other details, see Table 9). In this case there was no need for an extra parameter in equation (3) for the intercept because it is extremely small (+0.009). We have argued elsewhere that these solvolyses are weak $k_s$ processes,[4] although a case has been made that they are 'essentially $k_c$'.[5f] Consistent with our interpretation, it has since been shown that 2NbOTs can undergo $S_N2$ reactions with anionic nucleophiles under conditions where 2-AdOTs does not.[22]

New $Y_{OTs}$ values are shown in Table 8. Values of $Y_{OTs}$ have now been obtained from three model solvolyses, of 1- and 2-adamantyl and 2-*endo*-norbornyl tosylates.[2,5b,6,24] As would be expected there is slightly imperfect agreement between the $Y_{OTs}$ values obtained by different procedures. Rather than disguise this minor problem by averaging the values, we have shown both values, *e.g.* the $Y_{OTs}$ values for ethanol[24a] and water (Table 8). The slightly low $Y_{OTs}$ value for water obtained in the present work (4.04 *cf.* 4.1) is probably due in part to experimental uncertainties and also to inadequacies in equation (3); from equation (2) we calculate a higher value for $Y_{OTs}$ (4.19).

Figure 1 shows the approximately linear relationship between $H_0$ and $Y_{OTs}$ up to 60% $H_2SO_4$ with a significant deviation for 70% $H_2SO_4$.

*Solvent Nucleophilicity* ($N_{OTs}$) *for Aqueous Sulphuric Acid.*—Solvent nucleophilicity ($N_{OTs}$) is defined by equation (4), a

$$N_{OTs} = \log(k/k_0)_{MeOTs} - 0.3Y_{OTs} \qquad (4)$$

rearranged form of equation (1) with $m = 0.3$ for solvolyses of methyl tosylate at 50 °C. It has recently been suggested[25a] that, instead of setting $m = 0.3$ for solvolyses of methyl tosylate, a higher $m$ value (as high as 0.55) should be used. For reasons presented elsewhere,[25b] we prefer to retain the present definition. Values of $N_{OTs}$ are given in Table 8, and a curved plot of $N_{OTs}$ *vs.* log $a_{H_2O}$ in shown in Figure 2.

**Table 9.** Application of $lN + mY$, equation (1), to standard solvolysis data for alkyl tosylates[a]

| Tosylate | $l$ | $m$ | Std. devn. in log $k$ | Corr. coefft. |
|---|---|---|---|---|
| Methyl | 1.00[b] | 0.30[b] | | |
| Ethyl[c] | 0.82 ± 0.03 | 0.39 ± 0.03 | 0.13 | 0.997 |
| Isopropyl[d] | 0.41 ± 0.09 | 0.58 ± 0.08 | 0.41 | 0.936 |
| 2-Pentyl[e,f] | 0.33 ± 0.08 | 0.74 ± 0.08 | 0.35 | 0.972 |
| Cyclohexyl[g] | 0.25 ± 0.06 | 0.77 ± 0.05 | 0.27 | 0.985 |
| 2-*endo*-Norbornyl[h] | 0.05 ± 0.02 | 0.72 ± 0.02 | 0.10 | 0.998 |
| 2-*endo*-Norbornyl | 0.00[i] | 0.69 ± 0.02 | 0.13 | 0.997 |

[a] The current standard solvents are the following eleven (see ref. 4): 80% ethanol–water (v/v); 50% ethanol–water (v/v); ethanol; acetic acid; formic acid; trifluoroacetic acid; methanol; water; trifluoroethanol *or* 97% trifluoroethanol–water (w/w); 70% trifluoroethanol–water (w/w); hexafluoropropan-2-ol *or* 97% hexafluoropropan-2-ol–water (w/w); the intercept was varied but it was usually less than 0.05. [b] By definition. [c] Data for only eight solvents available; fluorinated alcohols excluded from the correlation; intercept −0.014. [d] Intercept −0.09; exclusion of data for trifluoroacetic acid gives $l = 0.54 \pm 0.06$, $m = 0.56 \pm 0.05$; corr. coefft. 0.979; intercept 0.04. [e] Data for only eight solvents available; ethanol, methanol, and 70% trifluoroethanol–water excluded from the correlation. [f] Intercept −0.24; exclusion of data for trifluoroacetic acid gives $l = 0.44 \pm 0.04$; $m = 0.70 \pm 0.04$; corr. coefft. 0.994; intercept −0.05. [g] Intercept −0.05; exclusion of data for trifluoroacetic acid gives $l = 0.34 \pm 0.04$; $m = 0.76 \pm 0.03$; corr. coefft. 0.995; intercept 0.03. [h] See also equation (3). [i] Assumed [see equation (2)].

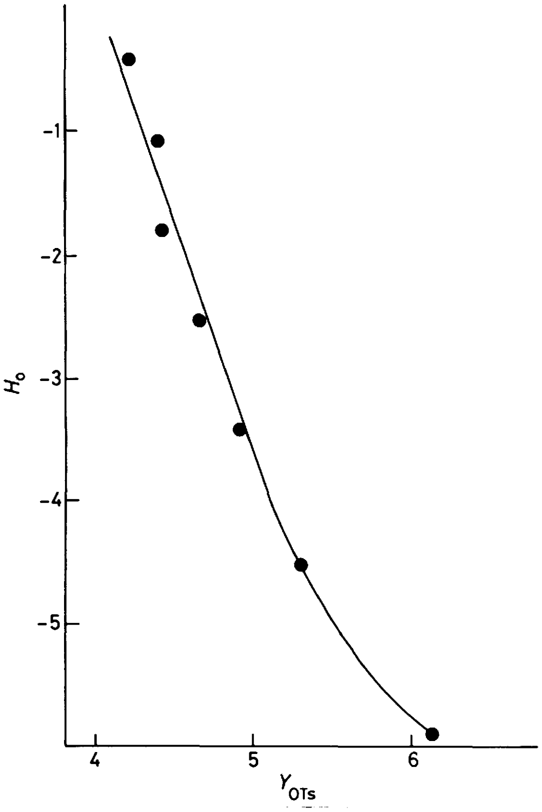


**Figure 1.** Plot of Hammett acidity function ($H_0$) *versus* solvent ionizing power ($Y_{OTs}$); data from Table 8; the equation of a line through the first six points is $H_0 = -3.76\ Y_{OTs} + 15.2$ (corr. coefft. 0.986)

A plot of $N_{OTs}$ *vs.* $Y_{OTs}$ (Figure 3) is close to linear except for 70% $H_2SO_4$. Hence a plot (not shown) of $H_0$ *vs.* $N_{OTs}$ is similar to Figure 1 and of log $a_{H_2O}$ *vs.* $Y_{OTs}$ is similar to Figure 2.

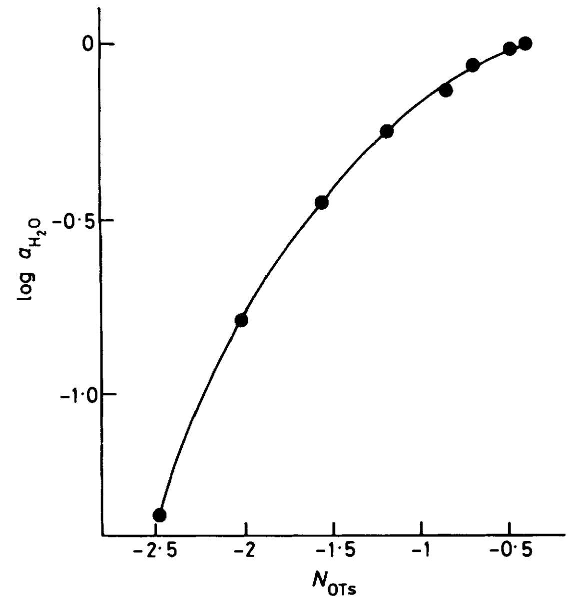


Figure 2. Plot of logarithm of water activity (log $a_{H_2O}$) *versus* solvent nucleophilicity ($N_{OTs}$); data from Table 8

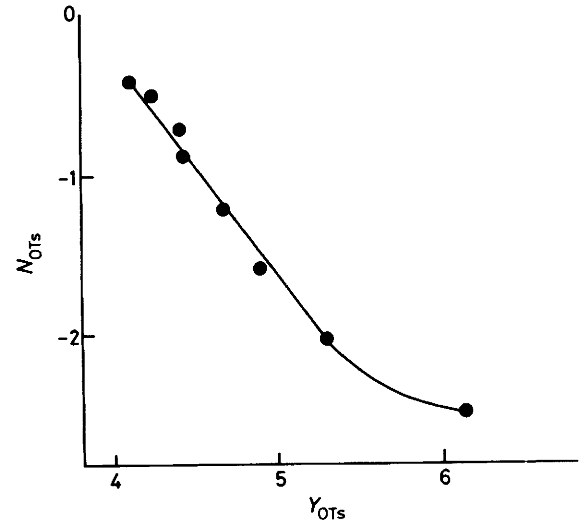


Figure 3. Plot of solvent nucleophilicity ($N_{OTs}$) *versus* solvent ionizing power ($Y_{OTs}$); data from Table 8; the equation of a line through the first seven points is $N_{OTs} = -1.37\ Y_{OTs} + 5.21$ (corr. coefft. 0.994).

*Comparisons with Other Solvolyses.*—A comparison between calculated [equation (1)] and observed rate–acidity profiles is shown in Figure 4. The calculated data were obtained from the $l$ and $m$ values and the small intercept terms given in Table 9, which were obtained from a standard data set of eleven solvolysis solvents (only four of which contain significant amounts of water and none of which contains $H_2SO_4$: see Table 9, footnote *a*). The general shapes of the three curves are reproduced well, even the flat part of the curve for ethyl tosylate between 60 and 70% $H_2SO_4$.

Agreement between calculated and observed values of log $(k/k_0)$ is satisfactory, except for isopropyl tosylate in 60 and 70% $H_2SO_4$. The more rapid increase in rate for secondary tosylates in these media may be due to protonation of these sulphonates; it appears to be of similar magnitude for all three secondary substrates (Table 4). To account quantitatively for this additional mechanistic pathway, an extra set of $l$ and $m$ values would be required. Kinetic data for solvolyses of substrates with positively charged leaving groups are accumulating, and these leaving groups may model alkyl–oxygen fission in protonated esters. In such cases $m$ may be close to zero,[27a,c] and the solvent dependence of rates for protonated leaving groups will depend almost entirely on the $lN$ term. The point at which there is upward curvature of the rate–acidity plots (Figure 4) will depend on $l$ and $k_0$, the reactivity of the protonated substrate in a non-acidic solvent (80% ethanol–water in our studies). As solvolyses of protonated substrates would be relatively more cationic in character than those of neutral substrates, the reactivity order Me < Et < secondary systems would be expected, consistent with the observed order of upward curvature of the plots (Figure 4).

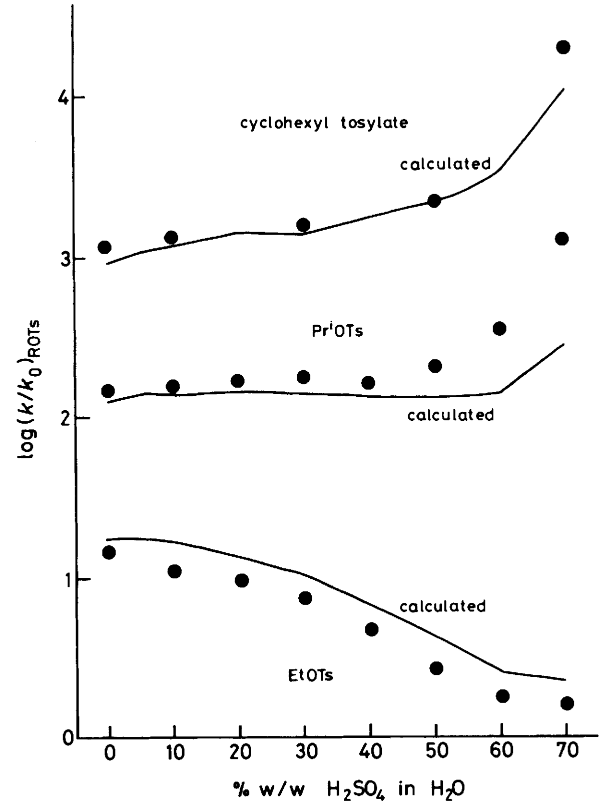
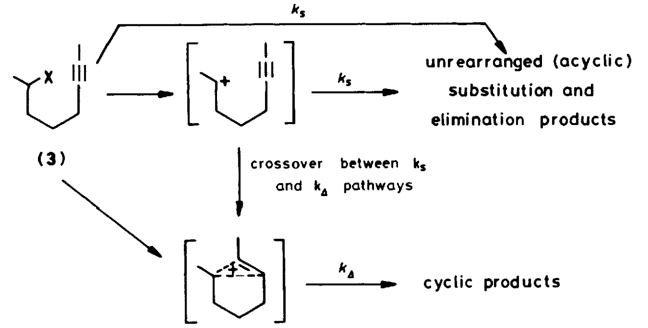


Figure 4. Comparison of calculated (curved plots) and observed (filled circles) values of log $(k/k_0)$ for cyclohexyl, isopropyl, and ethyl tosylates in aqueous sulphuric acid mixtures; kinetic data from Tables 3 and 4; calculated data from Table 9 and $k_0$ values from references 2 and 26.

Another application of the new $Y_{OTs}$ and $N_{OTs}$ values (Table 4) is the calculation of relative rates of competing reactions. If a direct relationship between rates and products is assumed,[28] product ratios can also be calculated. Sulphonates of oct-6-yn-2-ol (3; X = OH) (Scheme) have been solvolysed in carboxylic acids and in aqueous sulphuric acid mixtures, and product ratios for cyclized ($k_\Delta$ process) and unrearranged ($k_s$ process) products have been reported.[29] The $k_s$ process can be closely modelled by solvolyses of the tosylate of pentan-2-ol ($l = 0.33$, $m = 0.74$; see Table 9). For the $k_\Delta$ process, expected values would be $l = 0$ and $m$ *ca.* 0.85, because for $k_\Delta$ solvolyses of 1-phenyl-2-propyl tosylate, $m = 0.82$.[28a] The $k_\Delta/k_s$ value is then given by equation (5), where $k_\Delta{}^\circ/k_s{}^\circ$ refers to a standard solvent.

$$\log(k_\Delta/k_s) = \log(k_\Delta{}^\circ/k_s{}^\circ) + 0.11\,Y_{OTs} - 0.33N_{OTs} \quad (5)$$



Scheme.

In the absence of sufficient kinetic data,[27b] we assume that $k_\Delta^\circ/k_s^\circ$ can be obtained from product ratios. As data for 80% ethanol–water are not available, we have chosen acetic acid as a temporary reference solvent, so $Y$ and $N$ values have been adjusted by adding 0.61 to $Y_{OTs}$ values ($Y_{OTs}$ for acetic acid is $-0.61$) and by adding 2.35 to $N_{OTs}$ values ($N_{OTs} = -2.35$).[2] Calculated and observed values of log $(k_\Delta/k_s)$ are shown in Figure 5.

The observed and calculated product ratios agree well for $HCO_2H$, $H_2O$, and 10—40% $H_2SO_4$ (Figure 5), but major deviations are observed for the higher wt. % $H_2SO_4$ mixtures (55—70%). Minor differences due to the different leaving groups are evident from the experimental data, but this is insufficient to account for the large deviations. A higher $m$ value (up to 1.0) for the $k_\Delta$ process could be justified from the very limited amount of experimental kinetic data available for (3; X = OTs),[29b] but this would raise all the calculated $\log(k_\Delta^\circ/k_s^\circ)$ values. An alternative explanation of the deviations is failure of the assumed rate–product correlation. Crossover between $k_s$ and $k_\Delta$ pathways could occur (see Scheme), particularly if a relatively open (not nucleophilically solvated) secondary cation were formed. From the standard formula [equation (13), ref. 2] and the rate of solvolysis of 2-AdOTs in 70% $H_2SO_4$ (given by log $k_0$ + $Y_{OTs}$), we estimate the magnitude of nucleophilic solvent assistance ($k_s/k_c$) to be only 1.4 for solvolysis of isopropyl tosylate in 70% $H_2SO_4$, *i.e.* these solvolyses are almost as close to limiting $S_N1$ ($k_c$) as trifluoroacetolyses, presumably because the higher ionizing power of 70% $H_2SO_4$ offsets the higher nucleophilicity. However, the relative rates of competing $k_s$ and $k_\Delta$ pathways are influenced more by lowering $N$ values than by raising $Y$ values [*e.g.* equation (5)]. Hence there will probably be examples where trifluoroacetic acid[25b,28a] and hexafluoropropan-2-ol[28a] will be superior to 70% $H_2SO_4$ for synthetic applications in which the $k_\Delta$ process is desired; the enormous cost advantage of the latter solvent for preparative scale work should also be emphasised.[29a]

## Conclusions

For aqueous sulphuric acid mixtures (0—60% w/w and possibly 70% w/w), solvolyses of alkyl sulphonates provide model reactions in which the kinetic effects of increased solvent ionizing power ($Y_{OTs}$) and reduced solvent nucleophilicity ($N_{OTs}$) can be separated to a large extent from the effects of acid catalysis. Values of $Y_{OTs}$ and $N_{OTs}$ correlate almost linearly with $H_0$ and provide a kinetic alternative to the usual 'thermodynamic' approaches to reactivity in strongly acidic media.

Substitution of values of $Y_{OTs}$ and $N_{OTs}$ into equation (1) can lead to useful correlations of experimental data. These correlations (Figures 4 and 5) are partially successful, and deviations from equation (1) in higher % $H_2SO_4$ solutions provide evidence for additional mechanistic pathways (see also ref. 7). By identifying anomalies, such correlations assist in the choice of further independent experiments. Independent supporting data for an additional pathway *via* solvolysis of protonated substrate in 70% $H_2SO_4$ are the $^1H$ n.m.r. shifts (Table 7).

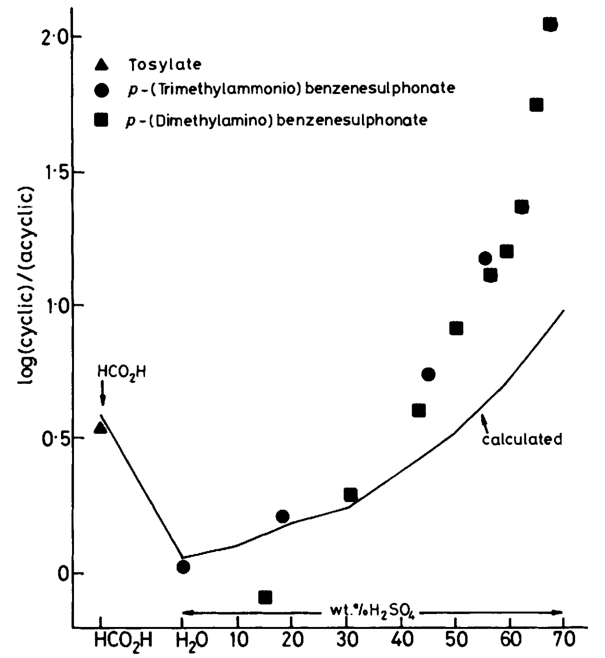


Figure 5. Comparison of calculated [curved plots based on equation (5)] and observed (filled circles, squares, and triangles for different leaving groups) product ratios for solvolyses of sulphonates of oct-6-yn-2-ol (Scheme); experimental data from ref. 29.

In preparative studies, mesylates are useful as water-soluble leaving groups, permitting further development of the use of aqueous sulphuric acid as a medium for increasing cyclization ($k_\Delta$ pathway) relative to solvolysis ($k_s$ pathway).

## Experimental

*Materials.*—Sulphonates were either commercially available (MeOTs, EtOTs, and EtOMs) or were prepared from the appropriate alcohol by standard methods.[5a] Sulphuric acid was B.D.H. A.R. grade (98%). Two sets of stock solutions were used throughout this work (one set for Table 2 and the other set for Tables 3 and 4).

*Kinetic Methods.*—Diverse methods were used for this work and many are summarised in footnotes to Tables 2, 3, and 6. The kinetic data in Table 4 were obtained from the ratios of $^1H$ n.m.r. peak heights of the singlet $CH_3$ in the starting material to the combined peak heights of the $CH_3$ in the starting material and product (observed over at least two half-lives), with the addition of a theoretical infinity point of zero. The n.m.r. instrument (Varian XL 100) was operated in continuous wave mode as described later and substrate concentrations were as low as 0.004M. Thermostatic control at 25 °C was achieved by heating a stream of compressed air, which had been cooled in ice. Although the heater setting on the instrument had only a coarse controller, once set correctly it was stable to within ±0.1 °C. Temperatures were checked by using a calibrated thermistor before and after each kinetic run. Temperature control at 10 °C required ice–salt cooling of a gas stream of dry nitrogen; stability $\pm$0.2 °C. For temperature control at 0 °C, a constant level of liquid nitrogen was the coolant.

*Extent of Protonation of Substrates.*—Changes in chemical shifts for ethyl mesylate in sulphuric acid (Table 7) were monitored by minor modification of the same stock solutions used for the kinetic studies. To the stock solution of acid (2.0 ml) in a 10 mm n.m.r. tube were added $D_2O$ (20 μl) (to provide a lock signal) and ethyl mesylate (5 μl; corresponding to *ca.* 0.02M). The mixture was then placed in a bath for ultrasonic treatment for 2 min before equilibration in the n.m.r. probe (Varian XL 100 instrument) for a further 10 min (temperature of the probe 30 °C). Accurate frequencies for the various peaks were obtained from single continuous wave scans by sweeping towards the peak maximum, stopping the pen at the peak maximum and then reading the frequency on the frequency counter. The sweep–stop process was repeated five times for each peak, and an average result was calculated. The accuracy of the procedure was judged from the range of each set of five readings for an individual peak (typically 0.4—0.8 Hz) and the coupling constant obtained from the two inner peaks of the quartet due to the $CH_2$ signal (7.0 $\pm$ 0.3 Hz for measurements in 50, 60, 70, 80, and 90% $H_2SO_4$; 6.3 Hz for 98% $H_2SO_4$). Errors in the quoted results are probably about 0.5 Hz.

$^{13}C$ N.m.r. spectra were investigated in less detail. Proton-noise-decoupled spectra were obtained with *ca.* 1M solutions by standard Fourier transform methods (5000 transients) using 5 mm n.m.r. tubes (XL 100 instrument) with dioxane added as internal reference and with $D_2O$ in a coaxial tube.

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