Kinetics and Mechanism of the Formation of Methacrylamide from 2-Methyl-2-sulphatopropionamide in Strong Acid Media

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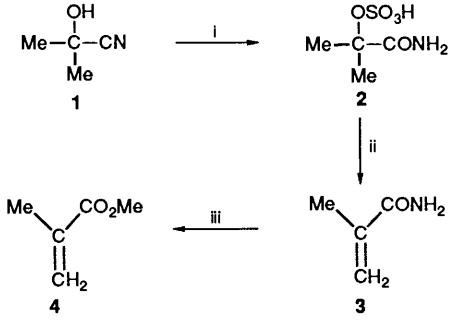
The kinetics and mechanism of the elimination of sulphuric acid from the sulphate ester of 2-hydroxy-2-methylpropionamide in 90–102% H_2SO_4 have been studied by multinuclear (^1H, ^2H, ^{13}C and ^{15}N) NMR spectroscopy. The results, which include activation parameters, influence of acid strength and kinetic isotope effects, are consistent with an E_2 elimination occurring from the protonated substrate and involving the hydrogensulphate anion as a base.

The industrial production of the commercially important monomer methyl methacrylate (**4**) involves the conversion of 2-hydroxy-2-methylpropionitrile (**1**) to methacrylamide (**3**) in *ca.* 100% sulphuric acid at elevated temperatures, followed by acid-catalysed methanolysis to give the product (Scheme 1).[1,2] The first stage of this process consists of two distinct reactions; a very rapid conversion of **1** to the β-sulphate ester of 2-hydroxy-2-methylpropionamide **2**, followed by a much slower elimination of sulphuric acid to give **3**. Despite its commercial importance the mechanism of this reaction has received little attention in the open literature.[3,4]

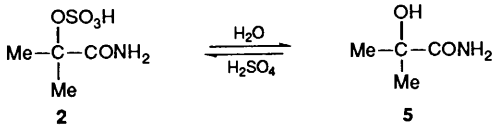


Scheme 1 *Reagents and conditions:* i, 100% H_2SO_4; ii, heat, 100% H_2SO_4; iii, H^+, MeOH

The first reaction occurs quantitatively and virtually instantaneously in 100% sulphuric acid, even at 0–5 °C, and has proved impossible to follow by means of conventional kinetic techniques, although a mechanism has been proposed on the basis of isotopic tracer studies.[5] By performing this reaction at low temperatures pure crystalline samples of **2** and/or 2-hydroxy-2-methylpropionamide (**5**) may be prepared, thus enabling a considerable volume of kinetic and mechanistic data concerning the elimination reaction to be acquired. The results of this investigation are discussed below.

Results and Discussion

In sulphuric acid solutions **2** is found to exist in equilibrium with 2-hydroxy-2-methylpropionamide **5**. In 95–100% sulphuric acid, at ambient temperature, both **2** and **5** are present in sufficiently high concentration to be detected by ^1H NMR spectroscopy, since they give rise to two distinct methyl signals. The coalescence temperature of these two signals in 98.5% sulphuric acid, as recorded on a 250 MHz spectrometer, was found to be 348 K, and the shift difference at low temperature, Δν, was 60 Hz. Since the ratio **2**:**5** under these conditions is *ca.* 1:1 we may apply the Gutowsky equation, $k_{Tc} = \pi\Delta\nu/2^{\frac{1}{2}}$. This



gives a value for k_{Tc}, the rate of interconversion of **2** and **5**, of 133 s^{-1} at the coalescence temperature, which is equivalent to a half-life of 5.2×10^{-3} s at 348 K.

To investigate the protonation of **2** and **5**, solutions in various acid concentrations were prepared and their ^{13}C NMR spectra recorded. The chemical shifts observed for the carbonyl and α-carbons are shown in Table 1 and are plotted as a function of acid concentration in Figs. 1 and 2.[6]

It is clear from the large downfield shift experienced by the carbonyl carbon (Fig. 1) that the amide function of **5** is fully protonated above 60% sulphuric acid.[7] In addition the ^{15}N

Table 1 ^{13}C NMR data for **2** and **5** in sulphuric acid at room temperature. All shifts are referenced to external dioxane at 67.4 ppm. (a) Variation of chemical shift with acid concentration for **5**; (b) variation of chemical shift with acid concentration for **2**.

	Chemical shift, δ(ppm)		Δδ	
% H_2SO_4	Carbonyl	α	Carbonyl	α
(a)				
0	183.93	73.87	0.00	0.00
10	184.01	74.06	0.08	0.19
20	184.09	74.10	0.16	0.23
25	184.28	74.14	0.35	0.27
30	184.40	74.12	0.47	0.25
40	184.85	74.05	0.92	0.18
50	185.30	73.72	1.37	−0.15
60	185.95	73.64	2.02	−0.23
70	186.03	73.75	2.10	−0.12
80	185.67	74.25	1.74	0.38
85	185.65	74.61	1.72	0.74
90	185.55	75.07	1.62	1.20
95	185.50	75.39	1.57	1.52
100	185.48	75.60	1.55	1.73
(b)				
96.0	181.73	87.53	0.00	0.00
97.0	181.68	87.56	−0.05	0.03
98.0	181.60	87.67	−0.13	0.14
99.0	181.51	87.86	−0.22	0.33
99.5	181.50	88.25	−0.23	0.72
100.0	181.37	88.34	−0.36	0.81
100.5	181.10	89.42	−0.63	1.89
101.0	181.12	89.46	−0.61	1.93
102.0	180.94	89.74	−0.79	2.21

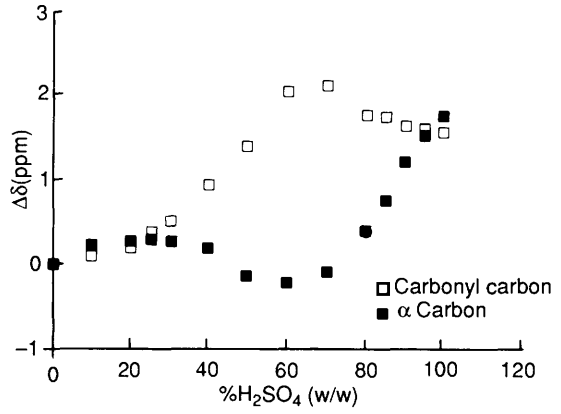


Fig. 1 Variation of ^{13}C NMR shift with acid strength for **5** in sulphuric acid

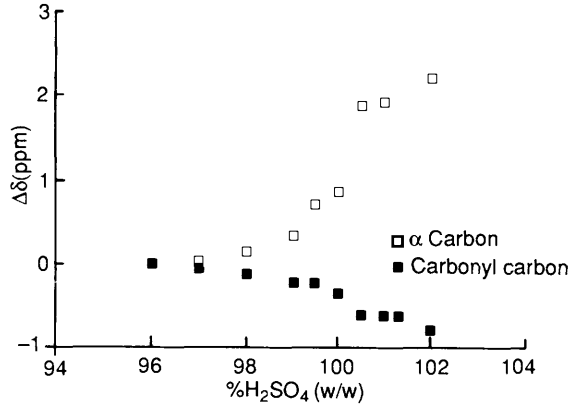
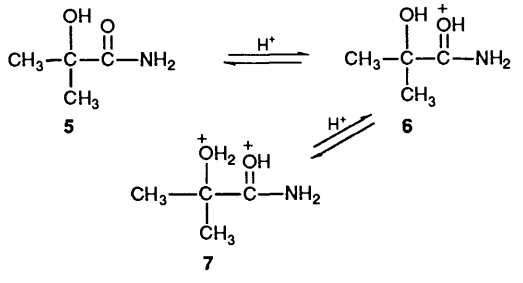


Fig. 2 Variation of ^{13}C NMR shift with acid strength for **2** in sulphuric acid

NMR spectrum shows a triplet resonance ($\delta_N = -251.5$ ppm relative to NO_3^-, $J_{NH} = 95$ Hz), indicating that this protonation occurs on the oxygen atom of the carbonyl group, to



form **6**, rather than on the nitrogen. It is possible to determine the ionisation ratio, I, of **5** to **6** from the NMR spectra using eqn. (1) (Table 2).

$$I = \frac{\delta - \delta_u}{\delta_p - \delta} \qquad (1)$$

We can therefore deduce the pK_a value appropriate to this protonation by plotting $\log_{10} I + H_0$ *vs.* $\log_{10}[H^+] + H_0$ according to the method of Bunnett and Olsen[8] (Fig. 3). Applying eqn. (2) to this plot leads to a value of -1.8 for the pK_a

$$\log_{10} I + H_0 = \Phi(H_0 + \log_{10}[H^+]) + pK_A \qquad (2)$$

of the amide function, which is in good agreement with the values of -1.3 found for isobutyramide,[9] and -1.8 found for methacrylamide.[7]

Although it is impossible to observe ^{13}C NMR spectra for **2**

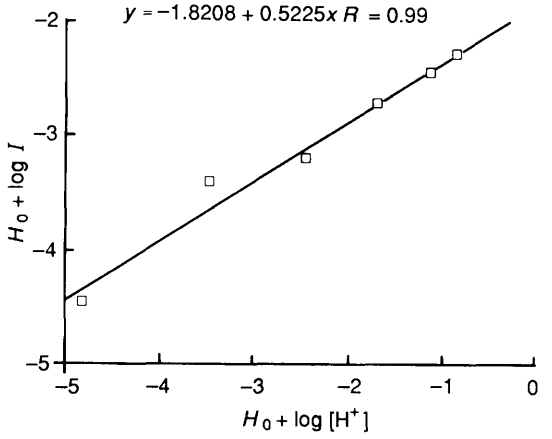


Fig. 3 Bunnett–Olsen plot for protonation of the amide group of **5**

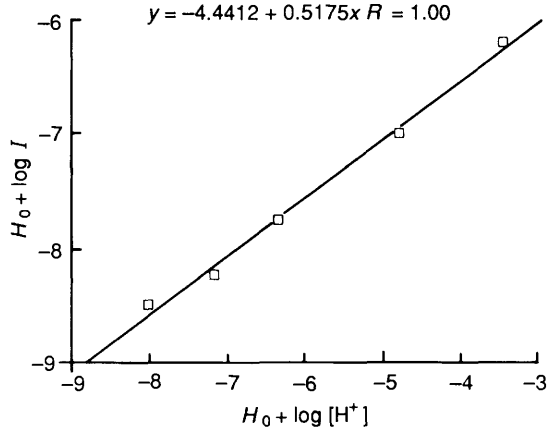


Fig. 4 Bunnett–Olsen plot for protonation of the hydroxy group of **5**

at these lower acidities, owing to its hydrolysis to **5**, it seems reasonable to suppose that it behaves in a similar fashion, and is thus fully protonated on the amide group above 60% sulphuric acid. Monoalkyl esters of sulphuric acid are themselves very strong acids,[10] and **2** will therefore be completely ionised in aqueous or weakly acidic solution. As anions of the form $R\text{-}OSO_3^-$ are much less basic than the amide function of **5**[10] it seems likely that **2** exists as the zwitterion **8** in moderately acidic media, with the sulphate group being protonated to form **9** only at higher acidities, probably in the region of 80–90% H_2SO_4.

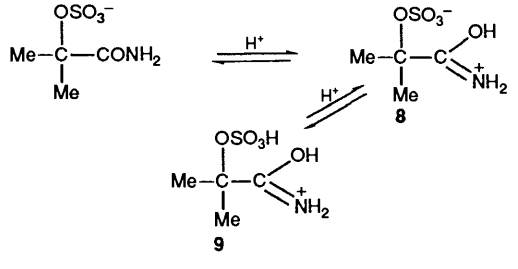


Fig. 1 also reveals the occurrence of a second protonation of **6** at very high acid concentrations, as indicated by the large downfield shift experienced by the α-carbon. This protonation occurs on the hydroxy group of **6** at 85% sulphuric acid (Fig. 1). The downfield shift of the α-carbon is consistent with the protonation of OH in **6** and is accompanied by an upfield shift of the carbonyl carbon. The origin of this latter effect is unknown, but it may be due to conformational effects within the doubly protonated molecule. Applying the Bunnett–Olsen method as above gives a pK_a value of -4.4 for the doubly protonated species (Fig. 4). A plot of chemical shift *vs.* acid

Table 2 Values of the ionisation ratio of (a) the amide group and (b) the hydroxy group of **5** at various acidities

% H_2SO_4 (w/w)	$-H_0$	$\log_{10}[H^+]$	$\log_{10} I$	$H_0 + \log_{10}[H^+]$	$H_0 + \log_{10} I$
(a)					
25	1.47	0.58	−0.8	−0.89	−2.3
30	1.82	0.67	−0.6	−1.15	−2.4
40	2.54	0.83	−0.2	−1.71	−2.7
50	3.41	0.94	0.2	−2.46	−3.2
60	4.51	1.03	1.1	−3.48	−3.4
70	5.92	1.10	1.5	−4.82	−4.5
(b)					
60	4.51	1.03	−1.7	−3.48	−6.2
70	5.92	1.10	−1.1	−4.82	−7.0
80	7.52	1.14	−0.2	−6.38	−7.8
85	8.29	1.12	0.1	−7.17	−8.2
90	9.03	1.00	0.5	−8.03	−8.5

Table 3 Kinetic data for the formation of **3** at various temperatures

	$k/10^{-4}$ s^{-1}	
T/K	98.5% H_2SO_4[a]	100% H_2SO_4[b]
343.0	0.82	1.5
348.0	1.62	2.3
353.0	2.33	5.0
358.0	4.33	7.0
363.0	8.67	14.6

[a] $E_A = 118 \pm 5$ kJ mol^{-1}, $\Delta S^{\ddagger} = 9 \pm 10$ J mol^{-1} K^{-1}. [b] $E_A = 109 \pm 10$ kJ mol^{-1}, $\Delta S^{\ddagger} = -2 \pm 10$ J mol^{-1} K^{-1}.

Table 4 Deuterium isotope effects for the elimination reaction in various acid strengths at 90 °C

% H_2SO_4	$k_H/10^{-4}$ s^{-1}	$k_D/10^{-4}$ s^{-1}	k_H/k_D
103	24.3	5.37	4.5 ± 0.1
100	13.1	2.54	5.2 ± 0.2
98	3.92	0.78	5.0 ± 0.1
95	1.48	0.35	4.2 ± 0.2

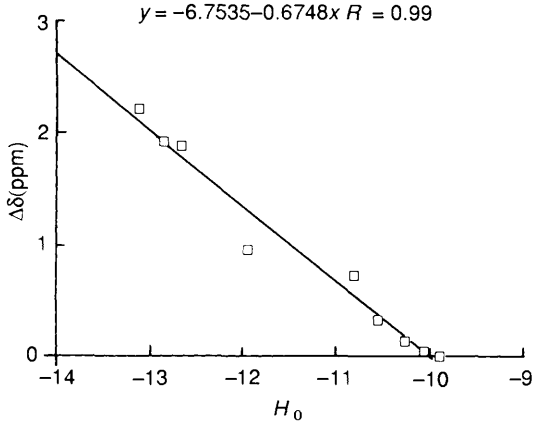


Fig. 5 Plot of chemical shift change *vs* H_0 for **2**

concentration for solutions of **2** in 95–102% sulphuric acid (Fig. 2) appears to indicate a protonation of the sulphate group. However, the value of H_0 as a function of acid concentration exhibits a similar pattern in this region, and a plot of chemical shift of the α-carbon *vs.* H_0 is in fact linear (Fig. 5), suggesting that this observation is due to medium effects rather than a protonation. From these results it appears that the three species present in acid concentrations of 90–100% are **6**, **7** and **9**, which are in equilibrium with each other. The interconversion of **6** and **9** is known to proceed by nucleophilic attack of the OH group of **6** on sulphur, without cleavage of the carbon–oxygen bond.[5] Above 100% sulphuric acid, *i.e.* in dilute oleum solutions, **9** is the only species present.

In order to assess the relative reactivity of **9** and **7** samples of **2** and **5** were dissolved separately in trifluoromethanesulphonic acid, which is of considerably higher acidity than 100% sulphuric acid,[11] and the elimination was monitored by ^{1}H NMR spectroscopy. Elimination from **2** occurred very rapidly indeed at 85 °C, with a half-life of 3.5 min, and 65% elimination was observed when the solution was left to stand for three days at room temperature. In contrast the solution containing **5** remained unchanged even after prolonged heating, although complete elimination could be effected by the addition of a small amount of 100% sulphuric acid. This shows clearly that elimination occurs only from **2**, presumably because the protonated OH group of **5** is a less efficient leaving group than HSO_4.

Arrhenius activation parameters for the elimination reaction were determined by measuring the pseudo-first-order rate coefficients at a series of temperatures in the range 70–90 °C, using a constant concentration of acid and constant initial substrate concentration throughout (Table 3). For example, the results shown in Table 3 were obtained using 98.5 and 100% (w/w) sulphuric acid and an initial concentration of 2.75% (w/w) in **2**. The reaction was monitored by ^{1}H NMR spectroscopy and good first-order behaviour was observed at all temperatures. These results demonstrate that the elimination conforms to the Arrhenius equation, to give $E_A = 118 \pm 5$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 9 \pm 10$ J mol^{-1} K^{-1} in 98.5% H_2SO_4. Similar data were obtained at an acid concentration of 100%.

The deuterium isotope effect for the elimination at 90 °C was determined at a series of acid concentrations (Table 4), using solutions containing 5% of **5** and 5% of hexadeuteriated **5**. The results are clearly consistent with a rate-determining C–H bond cleavage, and the isotope effect appears to be essentially independent of acid concentration (95–103%).

The rate of elimination was also found to be sensitive to the concentration of sulphuric acid employed, as shown in Table 5. These results were all obtained at 85 °C, using an initial concentration of 3% (w/w) of **2** in the acid media. The H_0 values used are obtained by extrapolating the data of Vinnik and Ryabova[6] to 85 °C, using the results of Tickle *et al.*[12]

From a plot of $\log_{10} k_{obs}$ *vs.* $-H_0$ (Fig. 6) it is clear that the reaction involves an equilibrium step whose equivalence point lies within the range of acid concentrations studied. It is possible to determine the ratio **9**:**7** from the 60 MHz NMR spectra, and if the values of k_{obs} are divided by the appropriate value of this ratio we obtain a value for k', the absolute rate constant for the reaction of **9**. A plot of $\log_{10} k'$ *vs.* $-H_0$ is linear (Fig. 7),

Table 5 Kinetic data for the formation of **3** at 85 °C in various acid strengths

% H_2SO_4 (w/w)	$-H_0$	$k_{obs}/10^{-4}$ s^{-1}	$\log_{10} k_{obs}$	X_2[a]	$k'/10^{-4}$ s^{-1}	$\log_{10} k'$
92.0	8.43	0.37	−4.43	0.06	6.0	−3.22
92.8	8.52	0.47	−4.33	0.08	6.1	−3.21
94.0	8.66	0.67	−4.17	0.11	6.3	−3.20
95.1	8.80	1.0	−4.00	0.15	6.8	−3.17
96.0	8.92	1.2	−3.92	0.17	7.2	−3.14
97.0	9.09	2.1	−3.68	0.21	10.0	−3.00
97.5	9.17	3.2	−3.49	0.32	10.1	−2.99
98.0	9.26	4.8	−3.32	0.41	11.8	−2.93
98.5	9.39	5.3	−3.28	0.45	11.7	−2.93
99.0	9.52	8.0	−3.10	0.67	12.0	−2.92
99.7	9.92	16.0	−2.80	0.9	17.8	−2.75
100.0	10.73	27	−2.57	1	27	−2.57
100.5	11.36	55	−2.26	1	55	−2.26
102.0	11.79	97	−2.01	1	97	−2.01

[a] X_2 = the fraction of total substrate present as **2**.

Table 6 Values of $\log_{10} k'$ at various acidities, and the appropriate values of $\log_{10}[H^+]$ and $\log_{10} a_{HSO_4^-}$ for the Bunnett–Olsen plot (Fig. 8)

% H_2SO_4 (w/w)	$\log_{10} k'$	$\log_{10}[H^+]$	$\log_{10} a_{HSO_4^-}$	$\log_{10}[H^+] + H_0$	$\log_{10} k' - \log_{10} a_{HSO_4^-}$
92.0	−3.22	0.945	0.952	−7.48	−12.61
92.8	−3.21	0.894	0.918	−7.63	−12.65
94.0	−3.20	0.830	0.856	−7.83	−12.71
95.1	−3.17	0.800	0.783	−8.00	−12.75
96.0	−3.14	0.749	0.708	−8.17	−12.77
97.0	−3.00	0.539	0.597	−8.55	−12.68
97.5	−2.99	0.392	0.525	−8.78	−12.69
98.0	−2.93	0.290	0.436	−8.97	−12.62
98.5	−2.93	0.187	0.320	−9.20	−12.64
99.0	−2.92	0.025	0.155	−9.49	−12.60
99.7	−2.75	−0.15	−0.126	−10.07	−12.54

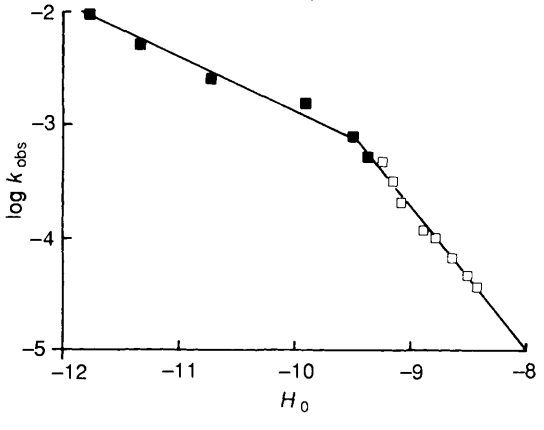


Fig. 6 Plot of $\log_{10} k_{obs}$ *vs.* acidity (H_0) for the elimination reaction at 85 °C

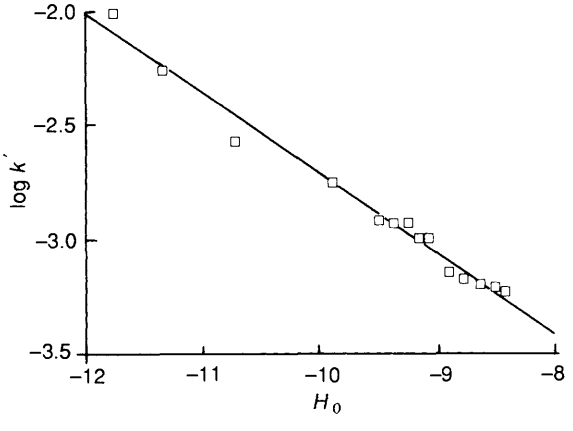


Fig. 7 Plot of $\log_{10} k'$ *vs.* H_0 for reaction of **9**

indicating that no further protonation of the substrate **9** occurs in this acidity range. This confirms that the shape of Fig. 2 is due to medium effects rather than a protonation of the sulphate group of **9**.

The method of Bunnett and Olsen[13] was applied to the results obtained in acid concentrations of 90–99.5% sulphuric acid, for which literature values of $\log_{10}[H^+]$ and $\log_{10} a_{HSO_4^-}$ are available (Table 6).[14] A plot of $(\log_{10} k' - \log_{10} a_{HSO_4^-})$ *vs.* $(H_0 + \log_{10}[H^+])$ was found to be linear (Fig. 8), with a correlation coefficient of 0.997, in accordance with eqn. (3),

$$\log_{10} k' - \log_{10} a_{HSO_4^-} = \Phi(H_0 + \log_{10}[H^+]) + \log_{10} k_0 \quad (3)$$

which applies for an A-2 mechanism involving one hydrogensulphate anion.[15] The appropriate plot for an A-1 mechanism, omitting the term in the hydrogensulphate activity, although apparently linear, gave a significantly poorer correlation.

The intercept of Fig. 8 gives a value for k_0, the value of the second order rate constant for reaction of **9** at infinite dilution, of 2.5×10^{-9} dm^3 mol^{-1} s^{-1}. The value of the slope parameter, Φ, obtained from Fig. 8 is a function of $f_9/f_\ddagger$, the ratio of the activity coefficients of **9** and the transition state. A negative value of Φ, as in this case (−0.6), implies that the activity coefficient of the transition state increases more rapidly with increasing acidity than does the activity coefficient of **9**. This in turn implies that the transition state is more highly solvated than the reacting substrate.

Conclusion

The reaction exhibits pseudo-first-order kinetic behaviour

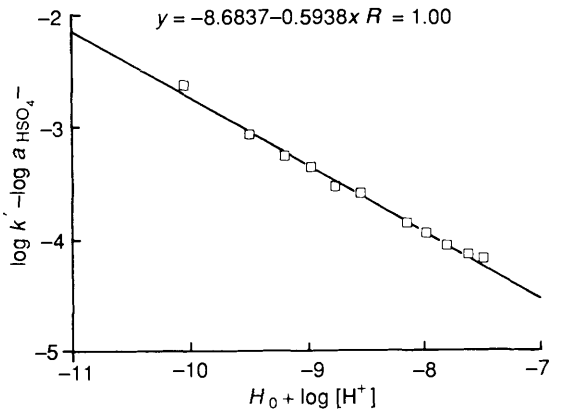
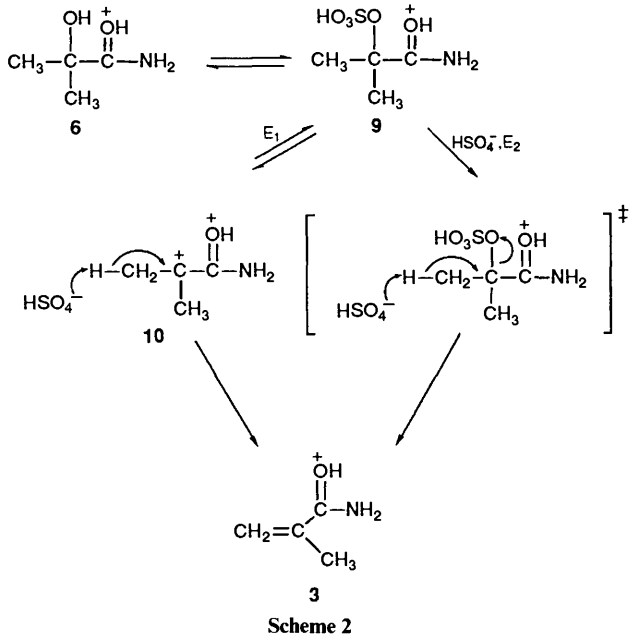


Fig. 8 Bunnett–Olsen plot for an A-2 mechanism, involving one hydrogensulphate anion

under all conditions studied, which is consistent with an E_1 or E_2 mechanism. The k_H/k_D values observed are indicative of a mechanism in which abstraction of a proton by a base is the rate-determining step.[16] The data concerning the protonation of **2** and **5** in acid solutions show that the two species present under our reaction conditions are **7**, the diprotonated form of **5**, and **9**, the monoprotonated form of **2**. Studies in trifluoromethanesulphuric acid, and the form of the plot of $\log_{10} k_{obs}$ *vs.* H_0 (Fig. 6), indicate that only the latter species is reactive. The reaction appears from Fig. 8 to be an A-2 process involving one hydrogensulphate anion as the base.



Scheme 2

In the light of the results presented above two possible mechanisms can be postulated, as shown in Scheme 2. In both cases **6** is converted to **9**, which may then react by two different pathways to give the product. Firstly, **9** may react with a hydrogensulphate anion in a concerted, E_2 elimination, in which abstraction of the proton by the base occurs synchronously with the formation of the double bond and departure of the hydrogensulphate leaving group. Alternatively, the reaction may follow an E_1 mechanism in which initial departure of the leaving group, to give the carbocation **10**, is followed by abstraction of a proton from **10** to give the product. It is clear from the values of k_H/k_D in Table 4 that in this case the abstraction of the proton would be rate-determining, as is found for the acid-catalysed E_1 dehydration of alcohols.[17] The activation parameters are consistent with either mechanism, although the E_1 pathway, involving the doubly-charged species **10**, might be expected to result in a more positive entropy of activation for the elimination, as observed in the acid-catalysed dehydration of carbinols.[18] This suggests that the E_2 mechanism is the more likely alternative, and two other pieces of evidence lend weight to this view. Firstly, our earlier experiments with ^{18}O-labelled **2**[5] showed no evidence for any loss of ^{18}O to the solvent, which would appear to rule out a pre-equilibrium step involving **9** and **10**. Secondly, the E_1 mechanism involves a doubly-charged intermediate **10** in the rate-determining step, and this would be expected to result in a positive value for Φ (Fig. 8), since one would expect **10** to be more highly solvated than the transition state leading to elimination.

None of the above evidence is entirely conclusive, however, and we cannot be certain which of the two possible mechanisms outlined above operates, although the concerted E_2 mechanism appears more likely.

Experimental

^{13}C NMR spectra were recorded on a Bruker AM 360 spectrometer operating at 90.56 MHz and referenced to external dioxane at 67.4 ppm. ^{15}N NMR spectra were recorded on a Bruker WM 250 spectrometer operating at 25.3 Hz, and ^2H spectra were recorded on the same instrument at 38.4 Hz.

Preparation of 2-Hydroxy-2-methylpropionamide **5**.—Compound **1** (Aldrich, 20 g, 0.23 mol) was added dropwise to 98% H_2SO_4 (100 cm^3) at 5 °C with vigorous stirring. The solution was diluted by the addition of water (3.5 dm^3) and neutralised with $CaCO_3$ (190 g). After filtration and removal of the solvent from the filtrate the product was extracted into acetonitrile, using a Soxhlet apparatus, and crystallised by partial evaporation of the solvent to yield **5** (14.5, 60%), m.p. = 96 °C; $\delta_H(D_2O)$ 1.5 (6 H, 2 × CH_3); $\delta_C(D_2O)$ 27.07 (CH_3), 73.87 (α-carbon) and 183.93 (C=O).

Preparation of [$^2H_6$]*2-Hydroxy-2-methylpropionamide*.—Hydrogen cyanide (5.5 g, 0.2 mol) was added to [$^2H_6$]acetone (10 g, 0.17 mol) at −10 °C in the presence of base to give deuteriated **1**. This was then treated as described above to give deuteriated **5** (9.4 g, 53%); $\delta_H(H_2O)$ 1.5 (6 D, 2 × CD_3).

Preparation of 2-Methyl-2-sulphatopropionamide **2**.—100% H_2SO_4 (40 g, 0.41 mol) in dry nitromethane (25 cm^3) was added dropwise, at 5 °C, to a solution of **1** (35 g, 0.4 mol) in nitromethane (250 cm^3) under a nitrogen atmosphere. When addition was complete the product separated as a solid, and the solvent was removed through a sinter stick. After being washed with nitromethane (2 × 100 cm^3) and dichloromethane (2 × 100 cm^3) the product was dried under high vacuum to yield **2** (68 g, 66%); $\delta_H(D_2O)$ 1.8 (6 H, 2 × CH_3); $\delta_C(D_2O)$ 25.02 (CH_3), 84.58 (α-carbon) and 179.93 (C=O).

Kinetic Measurements.—The substrate, either **2** or **5**, was dissolved in cold sulphuric acid of the appropriate concentration. Ten NMR tubes containing each reaction mixture were immersed in a thermostatted oil-bath, set to the required temperature, and removed at known intervals of time. The extent of reaction was determined from the ratio of the olefinic integral to the methyl integral in the ^1H NMR spectra, using eqn. (4), where x = olefinic integral and y = total methyl

$$\% \text{ Reaction} = 100\{3x/[y + (1.5x)]\} \quad (4)$$

integral. Rate coefficients were obtained from plots of ln (100 − % reaction), equivalent to ln [starting material], *vs.* time using a linear regression programme.

k_H/k_D values were obtained by carrying out this same procedure on solutions containing equal amounts of **5** and the hexadeuteriated compound, and analysing both the ^1H and ^2H NMR spectra.

Preparation of Sulphuric Acid Solutions.—Sulphuric acid solutions of appropriate concentration were prepared from commercial 98% H_2SO_4 (BDH) by the addition of either water or commercial oleum (BDH). The H_0 value of the solution was determined at 25 °C, using 2,4,6-trinitroaniline as an indicator, and compared with literature values.[6]

Acknowledgements

We thank Drs. J. Paton and T. O'Donoghue of ICI Chemicals and Polymers Ltd, for advice and technical support, and the SERC for financial support (to C. J. L.).

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Paper 0/02534H
Received 6*th June* 1990
Accepted 16*th November* 1990