# A 1H Nuclear Magnetic Resonance Study of the Protonation of Methacrylamide and of the Tautomerism of Its Cation

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Chemical shifts of the methyl and the vinyl protons of methacrylamide in sulphuric acid–water mixtures have been measured. The resonance of the methyl protons shifts downfield by 0.07$_5$ p.p.m. up to 60% acid and then remains virtually unchanged up to 100% acid. The resonances of the vinyl protons show large downfield shifts (the *cis*-proton by 0.55 p.p.m. and the *trans*-proton by 0.52 p.p.m.) up to 60% acid and then a substantial further shift to low field of 0.08 p.p.m. between 60% and 100% acid. This indicates a redistribution of charge in the cation, consequent upon the conversion of the *N*-protonated cation into the *O*-protonated cation. Half-conversion occurs in 78.5 ± 1.5% acid.

It is well known that the n.m.r. evidence on the structure of amide cations is apparently contradictory, since the spectra show rapid NH exchange in dilute acid, which can only be ascribed to the formation of the *N*-protonated form, and indisputable emergence of the *O*-protonated form in anhydrous acids (*e.g.* sulphuric, fluorosulphuric, and ' magic ' acid) for all simple amides.[1] On the basis of this, it has been widely held that the dominant form of the protonated amide is the *O*-protonated form, while only a small proportion of the *N*-protonated form is present, which causes rapid exchange of the NH protons with the medium on the n.m.r. time scale. Owing to this exchange, the fraction of the *N*-protonated form could never be obtained from the n.m.r. spectra of the amide group itself. Ultraviolet spectra, however, show that the protonation of some simple amides (*e.g.* benzamide[3] and methacrylamide[2]) in sulphuric acid up to 60% is followed by a further spectral change at higher acid concentrations, which has been ascribed to the tautomeric change of the *N*-protonated cation into the *O*-protonated cation.[2,3] In principle, this tautomeric change should also have an effect on the n.m.r. chemical shifts of the nuclei contained in the organic radical R [equation (i)]. For most ordinary amides studied so far these shifts appear to be very small[4] and could easily be dismissed as being due to an unspecified ' medium effect '. In this paper we report 1H n.m.r. chemical shifts for methacrylamide in solutions ranging from pure water to 100% sulphuric acid, which show undoubted evidence for the tautomeric change in the cation structure in the range 60—100% sulphuric acid.

$$R - C \overset{O}{\underset{NH_3^+}{\diagdown}} \quad \rightleftharpoons \quad R - C \overset{OH}{\underset{NH_2}{\diagdown}}^+ \qquad (i)$$
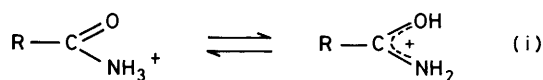
1H N.m.r. chemical shifts for methacrylamide in sulphuric acid–water mixtures (relative to t-butylammonium ion)

% H$_2$SO$_4$	$\Delta\delta_{Me}$	$\Delta\delta_{cis}$	$\Delta\delta_{trans}$	Notes
0	0.572	4.424	4.145	a
4.0	0.571			a
8.8	0.57			b
20.0	0.575			a
28.5	0.599	4.610	4.347	a
37.3	0.617	4.723	4.464	a
48.5	0.642	4.848	4.547	a
55.8	0.648	4.921	4.625	a
60.5	0.64$_5$	4.98$_5$ ^{c}	4.67 ^{c}	b
62.5	0.64$_5$	4.96$_5$ ^{d}	4.66$_5$ ^{d}	b
66.4	0.64$_5$	4.99	4.67$_5$	b
74.7	0.644	5.023	4.700	a
77.1	0.64$_5$	5.01$_5$	4.69$_5$	b
85.2	0.641	5.041	4.724	a
90.46	0.641	5.058	4.735	a
100.0	0.65	5.06	4.75	b

^{a} Obtained on the Brüker HXE 90 MHz spectrometer. ^{b} Obtained on the Perkin–Elmer EM 360 spectrometer. ^{c,d} The two values were averaged in calculating the total shifts between 0 and 60% acid and between 60 and 100% acid.

Experimental

Materials.—Methacrylamide was a commercial sample (Aldrich) and was recrystallized before use. Sulphuric acid solutions were made up by dilution of the 98% AnalaR acid and their concentrations were determined by titration with standard alkali. The 100% sulphuric acid was made up by mixing the 98% acid with oleum until a maximum in the freezing point (+10.46 °C) had been reached.

The solutions of methacrylamide were made up to a concentration of 0.1M, which was sufficient for accurate recording of the resonances, but not too high to change the concentration of the acid medium significantly.
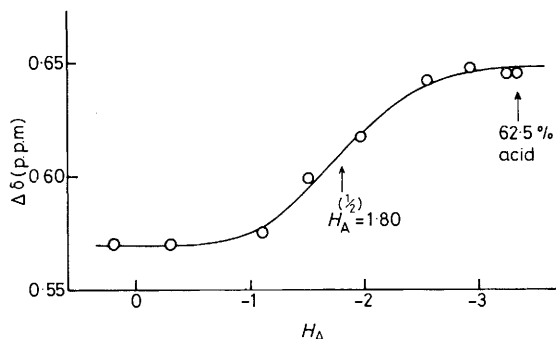
N.m.r. Spectra.—Two spectrometers were used: a Brüker HXE operating at 90 MHz (which gave direct readings of chemical shifts to three decimal places) and a Perkin–Elmer EM 360 operating at 60 MHz (for which chemical shifts were read off the spectra to an accuracy of ±0.005). t-Butylammonium sulphate was used as an internal reference in all

the mixtures (as in ref. 4). Its singlet resonance † was also used as the locking signal for the Brüker spectra, which often necessitated higher concentrations than in experiments performed on the Perkin–Elmer spectrometer. As a result, the overall accuracy of the chemical shifts obtained on the Brüker spectrometer is probably no higher than that obtained on the Perkin–Elmer EM 360. All measurements were carried out at room temperature.
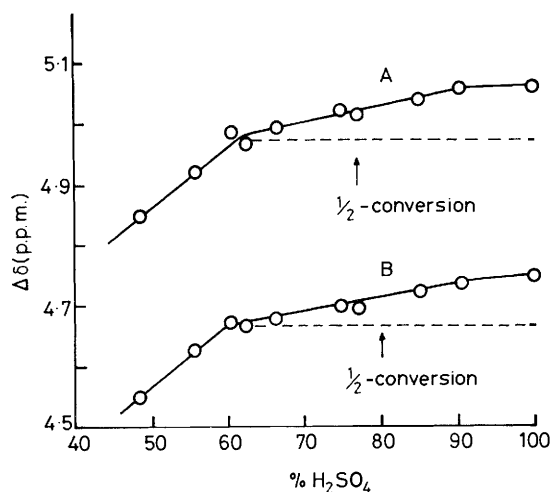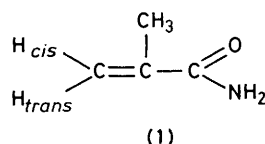
Results and Discussion

The results are given in the Table. The chemical shifts of the
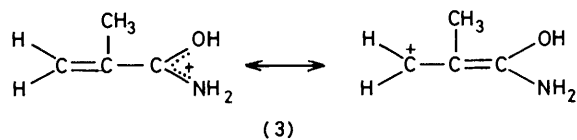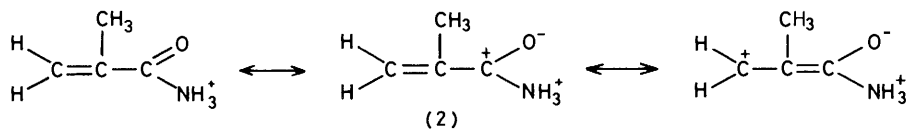
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† The chemical shift of this resonance [relative to internal sodium 2,2-dimethyl-2-silapentane-5-sulphonate (DSS)] changes slowly from δ 1.16 ± 0.02 in dilute acid to 1.26 in *ca.* 70% acid, and then more rapidly to 1.45 ± 0.02 in 100% acid, owing to the desolvation of the ammonium group.

Figure 1. Chemical shifts of the methyl protons of methacrylamide (relative to t-butylammonium) plotted against the H_A acidity function

(1)

Figure 2. Chemical shifts of the vinyl protons of methacrylamide (relative to t-butylammonium) in concentrated sulphuric acid: A, cis-proton; B, trans-proton

ence shows the familiar sigmoid shape, with a clear limiting value reached at ca. 60% acid. The point of half-protonation corresponds to an H_A value of -1.80, in close agreement with the pK_{AH^+} at 25 °C of -1.82, obtained for this amide spectrophotometrically.[2] A plot of log(ionisation ratio) vs. H_A was not attempted, because of too few points in the region of rapidly changing ionisation ratios and the low relative accuracy. The overall change in the chemical shift for these protons caused by protonation is only 0.07_5 p.p.m., rather smaller than that of the methyl protons of isobutyramide (0.15 p.p.m.) or of trimethylacetamide (0.13 p.p.m.).[4] This is due to the greater polarizability of the vinyl group as compared with that of saturated aliphatic groups. Significantly, and probably for the same reason, there is virtually no change in the chemical shift of the methyl group resonance beyond 60% acid.

The Vinyl Proton Resonances.—The two vinyl proton resonances, due to cis- and trans-protons in structure (1), have been assigned according to the degree of broadening by coupling to the methyl protons: the cis-proton resonance would be expected to be broadened less than the trans. On this basis the lower field resonance is due to the cis-proton. Both resonances shift downfield due to protonation (i.e. up to 60% acid) to a similar degree: the cis-signal by 0.55 p.p.m. and the trans by 0.52_5 p.p.m. This is almost three times as much as the protonation shift of the formyl proton in formamide,[6] which is α to the amide group, but is closely similar to the shift caused by protonation of the vinyl proton in trans-cinnamic acid, which has been determined as 0.52 p.p.m. [change between $(CD_3)_2SO$ and D_2SO_4].[7]

Both vinyl resonances show a sigmoid dependence on the H_A acidity function like the resonance of the methyl protons, but data are not obtainable over part of the range (see Table) because of the overlapping peak of the solvent protons, which moves downfield across the vinyl region with increasing acidity. The relative accuracy of the shifts is greater, however, than for the methyl protons because of the bigger changes involved and therefore a plot of the logarithms of the ionisation ratios, defined as $(\Delta\delta - \Delta\delta_B)/(\Delta\delta_{BH^+} - \Delta\delta)$,[4] versus H_A was attempted. There is reasonable agreement between the values from the two sets of data and a common straight line could be drawn through the points. Its slope, by least squares, is -0.84 ± 0.05, and the intercept on the H_A axis is -1.82, in excellent agreement with the value estimated from Figure 1 and with the pK_{AH^+} value obtained spectrophotometrically.[2]

(2)

(3)

methyl protons and those of the vinyl protons show different characteristics and will be discussed separately.

The Methyl Proton Resonance.—The chemical shifts of the methyl protons have been plotted in Figure 1 against the H_A acidity function, as corrected recently[2] to more negative values (by 0.1 unit) than earlier measurements.[5] The depend-

Chemical shifts of the vinyl protons do not remain constant above 60% acid, but show a substantial further shift to low field, with a tendency to level off above 90% sulphuric acid. The shifts are plotted against percentage sulphuric acid in Figure 2. The dotted lines represent the shifts of the fully protonated amide and the further downfield shifts are 0.08_5 p.p.m. for the cis- and 0.08_3 p.p.m. for the trans-proton, i.e.

they are equal within the limits of error and as big as the total protonation shift of the methyl protons. These shifts can be explained by an increasing deshielding of the β-carbon in the tautomeric change of the cation structure from N-protonated in 60% acid to O-protonated in 100% acid. It should first be recognized that the much greater downfield shift of the vinyl protons on N-protonation, as compared with the shift of the methyl protons, is due to a resonance spreading of the positive charge in the N-protonated cation between the carbonyl carbon and the β-carbon (2). The canonical structure showing the positive charge on the β-carbon arises as a result of charge repulsion from the protonation positive charge, which itself cannot be formally delocalised. When the tautomeric change takes place to the O-protonated form, the limiting resonance forms are (3), and the protonation positive charge is partially transferred from the O-protonated amide group to the β-carbon. There is no charge separation here and the deshielding of the β-carbon is therefore greater in this form. No significant change of charge density on the α-carbon is expected upon tautomerisation, which is reflected in the unchanging chemical shift of the methyl resonance relative to t-butylammonium.

The accuracy of the measurements is not sufficient for a calculation of reliable quotients, $Q_T = [O\text{-protonated}]/[N\text{-protonated}]$, with changing acid concentration, but the concentration at half-conversion can readily be estimated as 78.5 (± 1.5)% sulphuric acid (this is an average of the two estimates in Figure 2). This is in very good agreement with the estimate of 79.5% acid at the point of half-conversion of the benzamide cation from N-protonated to O-protonated, which was obtained from spectrophotometric measurements.[3] Likewise, the conversion is very approximately 90% in 90% acid. It is in this acid concentration that the first sign of the NH proton resonances of the O-protonated cation appears as a broad absorption. In 100% sulphuric acid this splits fully into two resonances, at δ 6.54 and 6.77, relative to the t-butyl-ammonium reference. Thus about 10% of the N-protonated form is sufficient to cause rapid NH exchange with the solvent protons in these media.

The results presented in this paper represent the first unambiguous n.m.r. evidence for the tautomeric change in the cation structure of amides from N-protonated in *ca.* 60% sulphuric acid to O-protonated in the 100% acid, which confirms u.v. findings.[2,3] The magnitude of the effect on chemical shifts is particularly large in the cations of methacrylamide because of extensive conjugation between the protonated amide group and the vinyl group, and the clear demonstration of the effects has been helped by the simplicity of the spectra.

References

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