Protonation on the Nitrogen Atom of a Substituted Carbamic Acid Ester

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EVIDENCE concerning the predominant position of protonation of amides and carbamic acid esters has so far been overwhelmingly in favour of protonation on the carbonyl oxygen.[1,2] An exception appears to be 2,2-dimethyl-6-oxoquinuclidine,[3] in which structural peculiarities enhance the basicity of the nitrogen atom compared with that of a normal amide, and prevent resonance stabilisation of the *O*-protonated form. We now present evidence for *N*-protonation of a carbamic acid ester.

Ethyl *NN*-di-isopropylcarbamate, when dissolved in 90—98% w/w sulphuric acid, gives an n.m.r. spectrum [(1) in Figure] in which the area and position of the broad peak A suggest the presence of one nitrogen-bound proton. If this is the case, the proton should exchange moderately rapidly with the solvent, and indeed the peak disappears when the solution in 98% sulphuric acid is warmed to 60°, or when the solution is made in 80% sulphuric acid, although separate experiments described below show that protonation is still essentially complete at this acidity. Cooling of the solution in 98% sulphuric acid produces a change in the fine structure of the resonance of the α-protons of the isopropyl groups (peaks B in Figure), which is to be expected if the coupling with a proton on the adjacent nitrogen atom is no longer completely time-averaged. A solution of the carbamate in fluorosulphonic acid also shows the peak A at temperatures below 0°, and gives a better resolved version of the splitting pattern of peak B in spectrum (1) in the Figure. No new peak appears even at −90°, in contrast to the observations of *O*-protonation in amides.[1] In 100% deuteriosulphuric acid at 20°, peak A is absent and peak B has the pattern shown in (2).

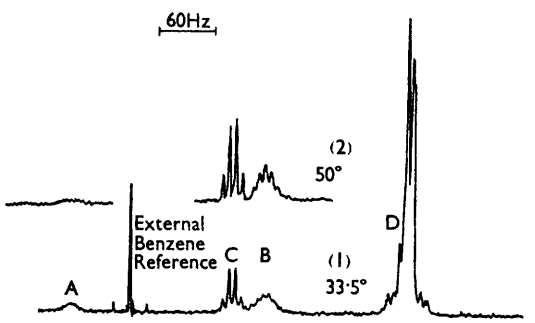

FIGURE. *N.m.r. spectra of ethyl* NN*-di-isopropylcarbamate in* 98% *sulphuric acid.*

In view of the difference in the acidity functions followed by oxygen-protonated amides and carbamates[4] on the one hand and tertiary anilines[5] on the other, we studied the protonation equilibrium of the present carbamate, which resembles the first class of compounds in structure, but the second in the

fact that its conjugate acid is a tertiary ammonium ion. A plot of the variation with acidity of the chemical shift difference between the methylene (centre of quartet C) and methyl (side peak of triplet D) resonances of the ethyl group for the range 28—98% sulphuric acid produced a sigmoid curve, from which the ionisation ratios at various acidities were derived as previously described,[4] and gave the following equation for the variation of the ratio of concentrations of conjugate acid and free base, I, with the Hammett acidity function[6] H_0,

$$\log I = -0{\cdot}83(\pm 0{\cdot}03)H_0 - 3{\cdot}31(\pm 0{\cdot}11)$$

which may be compared with the result[4] for the *O*-protonated[2] ethyl *NN*-dimethylcarbamate;

$$\log I = -0{\cdot}67(\pm 0{\cdot}04)H_0 - 3{\cdot}11(\pm 0{\cdot}16)$$

Graphical analysis of the ionisation data[5] for *NN*-dimethyl-2,4,6-trinitroaniline gives in contrast

$$\log I = -1{\cdot}34\,H_0 - 6{\cdot}66$$

The closer comparison with the former model compound supports in a rather direct way the conclusion[7] that the possible specific hydration of substituted ammonium ions is not in itself a good indication of acidity function behaviour.

The observation that in this case the introduction of bulky substituents on the nitrogen atom gives rise to a shift of the site of protonation from oxygen to nitrogen led us to prepare *NN*-di-isopropylacetamide and *NN*-di-isopropylbenzamide and to record the n.m.r. spectra of solutions of these compounds in 98% sulphuric acid. However, neither gave a peak attributable to a nitrogen-bound proton and in both cases separate methyl resonances for the two isopropyl groups were observed, which suggests restricted rotation about the carbonyl carbon–nitrogen bond due to protonation on oxygen.[1]

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