Ultraviolet Spectral Properties of Protonated Amides; the Question of the Site of Protonation

By H. Benderly and K. Rosenheck*

(Polymer Department, The Weizmann Institute of Science, Rehovot, Israel)

Summary Acidity dependent changes in the π–π^* and n–π^* absorption bands of aliphatic amides indicate that the N-protonated species constitutes no more than a very small fraction (*ca.* 10^{-3}) of the total protonated amide.

NUCLEAR magnetic resonance studies of amides in strong acids have established that in concentrated acid the carbonyl oxygen is the site of protonation.[1–3] No conclusive evidence has appeared so far for the existence of the *O*-protonated cation as the dominant form in dilute acid, although this was assumed to be the case.[1,2] Recently, however, it has been pointed out that the n.m.r. data in dilute to moderately concentrated acid are also consistent with *N*-protonation.[3,4] We present evidence, based on the u.v. absorption spectra of amides, which is in disagreement with the latter proposition.

The two lowest energy absorption bands of amides, in both aqueous and nonaqueous solutions, are a weak n–π^* transition, ϵ *ca.* 100, and a relatively strong π–π^* transition, ϵ *ca.* 8000.[5] Both originate in carbonyl transitions that have been strongly perturbed by the nitrogen $2p$ orbital participating in the delocalized π system extending over the N,C, and O atoms.[6] Thus, while in propionaldehyde the n–π^* band is located at 37 kK (270 nm) and the π–π^* band at 68 kK (147 nm),[6] in amides the n–π^* transition is blue-shifted to about 45 kK (222 nm) and the π–π^* transition is red-shifted to 50 to 58 kK (173–200 nm).[5,6] The delocalized nitrogen $2p$ orbital is the only orbital not participating in σ-bonding with the neighbouring atoms, and will necessarily be the one involved in the bond to the incoming proton, if protonation occurs on the nitrogen. In this event the nitrogen will effectively become decoupled from the carbonyl part of the chromophore, the spectral consequence being a reversal to the spectral properties of a simple carbonyl group, *i.e.* a large red-shift of the n–π^* band and a large blue-shift of the π–π^* band. The latter would be shifted beyond the solvent cut-off, and any remaining absorption in this region could be assigned to a weak carbonyl n–σ^* transition,[6] with an intensity at most $\frac{1}{5}$ of that of the amide π–π^* band.

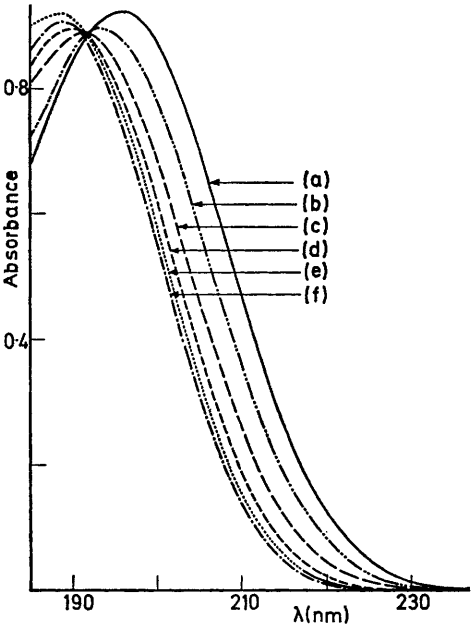

FIGURE 1. *The π–π^* absorption band of* NN-*dimethylacetamide,* (10^{-3} *mol* l^{-1}) l = 0·1 *cm in sulphuric acid of concentrations:* (*a*) 0%; (*b*) 7%; (*c*) 17%; (*d*) 30%; (*e*) 52%; (*f*) 60%.

The spectra of the π–π^* region of simple aliphatic amides† in sulphuric acid solution do not confirm this prediction.

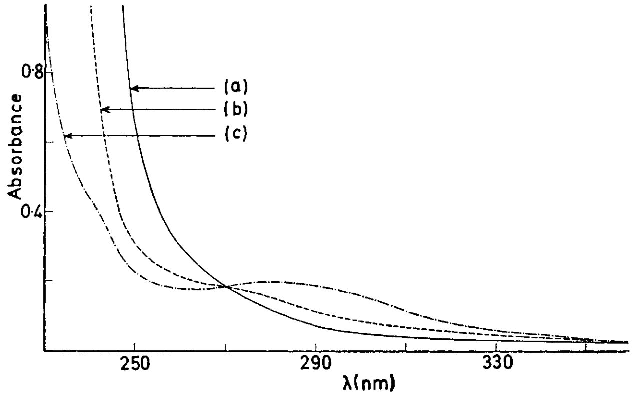

FIGURE 2. *The end absorption region of* N-*methylacetamide,* (2 *mol* l^{-1}) l = 5 *cm in sulphuric acid of concentrations:* (*a*) 0%; (*b*) 30%; (*c*) 60%.

In a typical example (Figure 1) there is only a small blue-shift of the absorption band of about 8 nm and no intensity change. This shift is much smaller than the one corresponding to the difference between the absorption maxima of the π–π^* band in amide and an unperturbed carbonyl group, *i.e. ca.* 25 to 50 nm. On the other hand, it is of the right magnitude for that expected in the case of *O*-protonation, involving a lone pair oxygen orbital.[6]

While the spectral data in the π–π^* region are thus inconsistent with the hypothesis of extensive *N*-protonation, the existence of *N*-protonated cations, in small quantities not easily detectable by the π–π^* spectral changes, has not been excluded. An estimate of the *N*-protonated species can be obtained from the absorption intensity in the n–π^* region of this species which should be situated at approximately its usual location for unperturbed carbonyl groups (see above). Under the conditions given in Figure 2 a weak absorption band is indeed detected at about 34 kK (295 nm). Assuming a molar extinction coefficient of *ca.* 10, a value constituting a typical lower limit for aldehydes or ketones,[7] the upper limit for the concentration of *N*-protonated amide is calculated to be *ca.* 2×10^{-3} mol l^{-1} and the ratio of *N*-protonated to *O*-protonated species is therefore *ca.* 10^{-3}. Consequently, these u.v. spectral data support the assumption[1,2] that the *O*-protonated cation is the dominant species in dilute acid.

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† *N*-Methylacetamide (purum, Fluka) and *NN*-dimethylacetamide (puriss, Fluka) were distilled once before use. Sulphuric acid was BDH, Analar grade. Spectra were recorded on a Cary Model 15 far u.v. spectrophotometer.

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