Spectrophotometric Confirmation of the Tautomerism of Amide Cations in Concentrated Sulphuric Acid

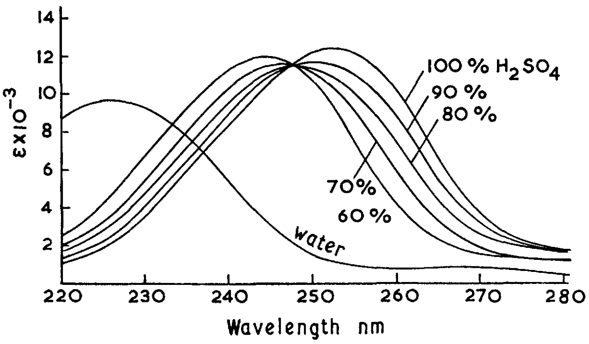
By M. LILER
(*School of Chemistry, The University, Newcastle upon Tyne* NE1 7RU)

Summary Ultraviolet absorption of benzamide in conc. sulphuric acid undergoes changes due to a shift of the tautomeric equilibrium of amide cations from *N*-protonated in 60% acid to *O*-protonated in 100% acid.

A SUGGESTION,[1] based on the pK_{BH^+} values of amides[2] and n.m.r. spectra,[3] that amides are *N*-protonated in aqueous acid, but become *O*-protonated in conc. and anhydrous acids, is now shown to be supported by u.v. spectra of benzamide in conc. sulphuric acid. It has been found that benzamide is fully protonated in 55—60% sulphuric acid, but that the maximum absorption undergoes a bathochromic shift at still higher acid concentrations. This was ascribed to a medium effect. The spectrum in 59·3% acid was shown[5] to be closely similar to that of unprotonated acetophenone in 50% acid, as expected for the *N*-protonated cation,[5] since replacement of Me by NH_3^+ has little effect on the u.v. spectra of many aromatic compounds.[6] Hantzsch[7] has earlier demonstrated the virtual identity of the u.v. spectra of benzamide and of ethyl benzimidate in 100% sulphuric acid and had concluded that the *O*-protonated cation of benzamide was present in that medium.

The published u.v. evidence thus being consistent with a tautomeric change of benzamide cations in 60—100% sulphuric acid, the u.v. spectra of benzamide were examined more closely in sulphuric acid solutions over that concentration range, using a Zeiss spectrophotometer PMQ II at 26 °C. Some absorption curves are shown in the Figure. It was confirmed that an absorption maximum at 244·5 nm is observed in 60% acid, which shifts at higher acid concentrations, giving a new maximum at 252·5 nm in 100% sulphuric acid. All absorption curves pass through an isosbestic point at 247·5 nm, thus demonstrating that the spectral changes are due to a shifting equilibrium. According to the u.v. spectra, the *N*-protonation and the tautomeric changeover equilibria of benzamide do not overlap seriously. Half-conversion of the *N*-protonated cation into the *O*-protonated cation occurs in *ca.* 80% sulphuric acid. The concentration dependence of the tautomeric equilibrium will be discussed elsewhere, in conjunction with n.m.r. spectra of [^{15}N]benzamide in the same media.

(*Received*, 24*th February* 1972; *Com.* 302.)



FIGURE

[1] M. Liler, *Chem. Comm.*, 1971, 115; *J.C.S. Perk. II*, 1972, in the press.

[2] M. Liler, 'Reaction Mechanisms in Sulphuric Acid Solutions,' Academic Press, London, 1971, pp. 107, 108, 134.

[3] A. Berger, A. Loewenstein, and S. Meiboom, *J. Amer. Chem. Soc.*, 1959, **81**, 62; G. Fraenkel and C. Franconi, *ibid.*, 1960, **82**, 4478; M. Liler, *J. Chem. Soc.* (*B*), 1969, 385; 1971, 334.

[4] J. T. Edward and S. C. R. Meacock, *J. Chem. Soc.*, 1957, 2000.

[5] J. T. Edward, H. S. Chang, K. Yates, and R. Stewart, *Canad. J. Chem.*, 1960, **38**, 1518.

[6] R. N. Jones, *Chem. Rev.*, 1943, **32**, 14; L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714.

[7] A. Hantzsch, *Ber.*, 1931, **64**, 667.