Formation of two Different Entities on Protonation of Formic Acid

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A REMARKABLE phenomenon was encountered in the protonation of formic acid in HF–BF_3 solution. The n.m.r. spectrum of the solution measured at −67° is given in Figure 1a. The low-field absorptions *I*, *II*, *III* are due to *O*-hydrogens and those at high field, *IV*, *Va*, *b*, to *C*-hydrogens. This was shown by measuring the spectrum of protonated DCO_2H under the same conditions (Figure 1b). The relatively complicated spectrum is thought to originate from two different ions present in the solution. Structures (A) and (B) are suggested.[1] Protons H_α and H_β in structure (A) are magnetically nonequivalent, and give rise to absorptions *I* and *III*, respectively (assignment on the basis of the coupling constants). In species (B)[2] the *O*-hydrogens are magnetically equal and cause absorption *II*.

The arguments in favour of this hypothesis are:

(i) Double-resonance experiments show that saturation of absorption *IV* causes the

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collapse of doublet *II* into one peak, while saturation of absorption *Va, b* reduces both doublets *I* and *III* to a single peak each.

(ii) The ratio of the intensities of the bands in the spectrum is roughly 1·7 (*I*) : 1·0 (*II*) : 1·7 (*III*) : 0·5 (*IV*) : 0·8 (*Va*).

(iii) The values of the coupling constant in absorptions *II* and *IV* are equal (J = 3·2 c./sec.), and the coupling constants of absorptions *I* and *III* (J = 3·2 and 13·9 c./sec., respectively) are equal to those of absorption *Va,b* (*Vb* is not observed directly, but from the double-resonance experiments and the chemical shift of the collapsed signal from *IV, Va,* and *Vb* at high temperature its presence and position are well defined).

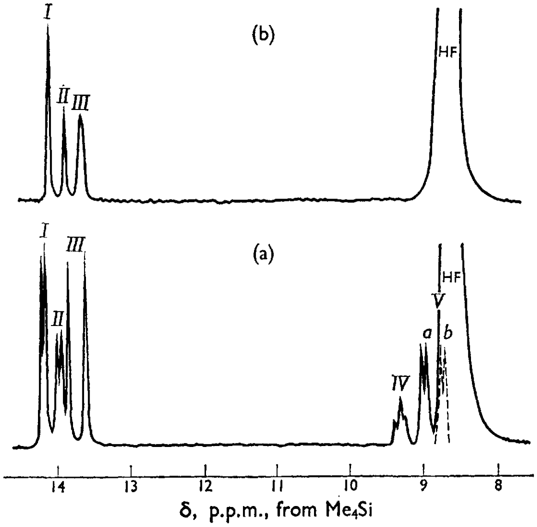
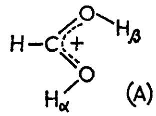
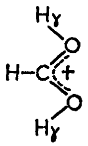


FIGURE 1. *N.m.r. spectra of protonated formic acid* (*a*) *and deuteroformic acid* (*b*) *in* $HF–BF_3$ *solution at* −67° (1·5 *moles/litre*; *pressure* BF_3 2·5 *atm*) *Doublet* Vb *not directly observed* (*see text*)



(A) (77%)



(B) (23%)

At higher temperature, proton transfer reactions set in, absorptions *I, II, III* begin to broaden and ultimately disappear, while the high-field absorptions collapse into one sharp line. Both the absence of any residual average coupling in this peak and the broadening of the HF peak indicate that the two species (A) and (B) are not directly interconvertible under the experimental conditions but that the process occurs *via* unprotonated formic acid, which is present in small concentrations and is not observed in the spectrum.

A surprising and intriguing fact is the very slow dehydration of protonated formic acid in both $HF–SbF_5$ and $HF–BF_3$ solutions, as compared with the reaction in sulphuric acid.

(*Received, October 24th,* 1966; *Com.* 816.)

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[1] An A-type structure has recently been suggested for dimethoxycarbonium ions; B. G. Ramsey and R. W. Taft, *J. Amer. Chem. Soc.*, 1966, **88**, 3058.

[2] In principle, other structures of the ion with magnetically equivalent protons—such as one protonated on the hydroxyl oxygen atom, $HCO{\cdot}OH_2^+$ —can be considered.