The N.M.R. Spectra of Protonated EtOH, MeOH, and H_2O in Solutions of HBr in CF_2Br_2–CD_2Cl_2

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Summary The ^1H n.m.r. spectra of mixtures of ROH (R = Et, Me, H) and HBr in CF_2Br_2–CD_2Cl_2 at −100 °C and below show signals at *ca.* 12—13 p.p.m. and −1·5 p.p.m. which are attributed to the species ROH_2^+ and HBr respectively.

Under appropriate conditions the species ROH_2^+ are sufficiently long-lived to give well resolved n.m.r. spectra. It has always been assumed that extremely strong acids were a prerequisite for such behaviour since observation of the ions was confined to such acid systems as HSO_3F,[1] HF–BF_3,[2] and HSO_3F–SbF_5–SO_2,[3] at low temperatures. Only with the last type of acid does the $-OH_2^+$ signal show the expected fine structure.

Most interest has naturally been shown in the parent oxonium (H_3O^+) cation in solution. Its presence as a distinct entity in solution was inferred many years ago from transport measurements in liquid SO_2–HBr–H_2O,[4] and more recently also from spectroscopic observations.[5,6] Conclusive evidence for the existence of a species with the symmetrical structure H_3O^+ came from the ^1H n.m.r. spectra in partially deuteriated HSO_3F–SbF_5–H_2O systems,[7] and latterly also from ^{17}O n.m.r. spectroscopy.[8]

We have now been able to achieve conditions under which these species are sufficiently long-lived to be observable by n.m.r. spectroscopy without having to employ superacids, *viz.* by use of HBr as the acid (in considerable excess over ROH) and CF_2Br_2 or CF_2Br_2–CD_2Cl_2 as a solvent (known to be a poor hydrogen bond acceptor).

Ethanol and HBr in CF_2Br_2 show a single (merged) sharp peak, $\delta(H) = 6{\cdot}34$ p.p.m., at temperatures above −40 °C. This broadens and shifts on cooling. At −100 °C the peak, centred at *ca.* 9·4 p.p.m., is very broad and barely distinguishable. The spectrum at −120 °C consists of broad bands at *ca.* 12·1 p.p.m. ($EtOH_2^+$) and at −1·14 p.p.m. (HBr), *i.e.*, upfield of Me_4Si (in addition to the alkyl proton signals). The system can be cooled further to −130 °C, but the peaks remain broad, 30 Hz for $EtOH_2^+$ and 9 Hz for HBr, and no fine structure of the former has so far been seen. This behaviour may be attributable to viscosity broadening and possibly to strong hydrogen bonding between $EtOH_2^+$ and Br^-.[6,9] The merging of the signals at higher temperatures is due to proton exchange between $EtOH_2^+$ and HBr.

Methanol is soluble in the mixed solvent CF_2Br_2–CD_2Cl_2. The system MeOH–HBr behaves in this solution in the same way as EtOH–HBr in CF_2Br_2, showing broad signals at *ca.* 12·1 p.p.m. ($MeOH_2^+$) and −2·28 p.p.m. (HBr) at −100 °C. The signals become sharper as the temperature drops.

Water by itself is virtually insoluble in CF_2Br_2–CD_2Cl_2 even when CD_2Cl_2 is in excess, but the accumulated Fourier transform spectra on very dilute solutions of H_2O–HBr show the same resolution into two resonances at temperatures below −100 °C; at −120 ° these signals are at *ca.* 13·0 p.p.m. (H_3O^+) and −1·37 p.p.m. (HBr). The identification of the low-field signal with H_3O^+ and ROH_2^+ follows from comparison with the positions of these signals in the superacid systems.[3,7]

The signal for HBr in CF_2Br_2 at −100 °C is at −2·80 p.p.m. This upfield location has been noted before in different systems.[10] The precise position of the signal is more sensitive to temperature and solvent than the ROH_2^+ signal. This variability may be due to HBr polymers. It is not attributable to the presence of HBr_2^- ions: the hydrogen dibromide ion has $\delta(H)$ downfield at 10·15 p.p.m. and this position is reported to be insensitive to either solvent or temperature changes.[11]

Raising the acidity of our system should slow down the exchange rate (and increase the residence time of the protons): indeed, the addition of SbF_5 to H_2O–HBr in CF_2Br_2–CD_2Cl_2 permits the separate signal for H_3O^+ to be observed at temperatures as high as −30 °C.

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