Evidence for the Existence of Long-lived H_3O^+ (Oxonium) Ions in Solution: N.M.R. Spectra of Isotopic Oxonium Ions in HSO_3F–SbF_5 ('Magic Acid') Systems

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Summary ^1H N.m.r. signals due to long-lived H_3O^+, H_2DO^+ (1 : 1 : 1 triplet), and HD_2O^+ ions are observed in partially deuteriated HSO_3F–SbF_5–H_2O systems in SO_2 or SO_2ClF solution, thereby providing unambiguous spectroscopic evidence for the existence of H_3O^+ ions without further hydration in solution.

Although the existence of the oxonium ion† H_3O^+ in crystals and in the gas phase has been firmly established for some years,[2] there has until now been no equally compelling direct physical evidence for the presence of H_3O^+ ions in solution. The strongest early indications that this species can exist in solution came from transport measurements on HBr + H_2O in sulphur dioxide solution.[3] The subsequently observed low-temperature vibrational spectra of such solutions[4] were found to be consistent with the presence of H_3O^+.

Measurements of the fractionation of deuterium between water and aqueous hydrogen ions by different experimental methods and the dependence of protolytic rates and equilibria on the deuterium content of aqueous acids indicate the presence of the grouping H_3O^+, with three equivalent hydrogen atoms.[5] However, they do not rule out that the aqueous hydronium ion is a species with further hydration. Neither i.r. nor n.m.r. spectra of aqueous solutions provide unambiguous supporting evidence for H_3O^+. Whilst the i.r. spectra[6] are not inconsistent with the existence of H_3O^+, the presence of extensive hydrogen bonding in aqueous systems causes vibrational spectra to be poorly characterised. The rapidity of proton transfer reactions always results in the appearance of only a single sharp signal in the proton resonance spectra of aqueous acids.[7]

In a more strongly acid medium, *viz.* sulphuric acid, the freezing-point depression caused by added water is normally interpreted in terms of the reaction (1). However, the

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^- \qquad (1)$$

freezing-point depression actually indicates the formation of less than two solute particles per molecule of water added.[8] This is *prima facie* evidence for incompleteness of reaction (1). In view of the more complete protonation of weaker bases than water, the result is more plausibly attributed to the reaction (2), implying an exceptionally

$$H_3O^+ + H_2O \rightleftharpoons H_5O_2^+ \qquad (2)$$

high tendency for a water molecule to stabilise the oxonium ion H_3O^+ by hydrogen bonding, so that there is competition between reactions (1) and (2). Going to an even more strongly acidic medium, reaction (2) may perhaps compete less effectively with the protonation of water by the acid.

Solutions produced by the addition of water to 'superacid' systems (HF–BF_3[9] and HSO_3F–SbF_5[10]) exhibit two distinct ^1H n.m.r. signals which have been attributed to the acid itself and to the oxonium ion H_3O^+. Whilst these observations imply that proton exchange between the acid and the other species is slow on the n.m.r. time scale, they do not strictly establish that the water-derived species is H_3O^+ rather than the ion $H_5O_2^+$ (or some other hydrate of H_3O^+ containing rapidly equilibrating, but non-equivalent, protons).[11]

We have investigated the nature of the cations produced in these systems further by examining the ^1H n.m.r. spectra of the partially deuteriated solutions. When deuterium oxide (0·16 mol.) is added to HSO_3F–SbF_5 (1 mol.: 0·7 mol.), or water (0·15 mol.) to DSO_3F–SbF_5 (1 mol. each), and the resulting solutions are diluted with a three to five-fold excess of sulphur dioxide or sulphuryl chloride fluoride (SO_2ClF), we observe that the ^1H resonance spectra at temperatures in the region 213—253 K contain the usual acid peak[10] at δ 9·8—11·1 relative to external Me_4Si, the precise position depending on the nature of the diluent, the degree of dilution, and on the temperature. The peak at δ 9·3—10·8 arising from the addition of water is split into three signals, separated by 0·054—0·059 p.p.m., which are fully resolved at 220 MHz. Two independent lines of evidence establish that these three signals correspond to the isotopic oxonium ions H_3O^+, H_2DO^+, and HD_2O^+.

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† In accordance with I.U.P.A.C. Rules,[1] the name 'oxonium' ion is taken to refer to the unsubstituted parent species H_3O^+. We follow general usage in applying the name hydronium ion to the solvated hydrogen ion in solution. We propose to reserve the term 'hydroxonium ions' for the specific species $H_5O_2^+$, $H_7O_3^+$, *etc.*

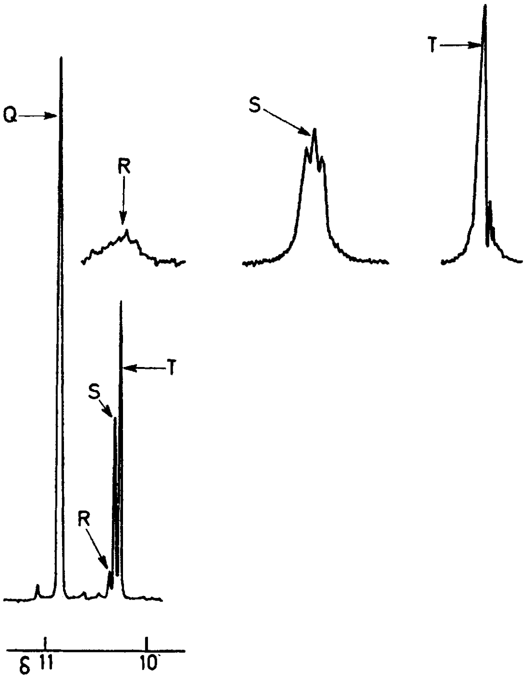

FIGURE. 220 MHz ^{1}H resonance spectrum of HSO_3F–SbF_5–D_2O (1 mol. : 0·7 mol. : 0·16 mol.) in SO_2 (4 vol.) at 229 K. (Scale-expanded signals inset. Q, HSO_3F; R, HD_2O^+; S, H_2DO^+; T, H_3O^+).

First, the relative intensity of the three peaks depends on the abundance (F) of deuterium in the oxonium ion. If one makes the assumption that there is random distribution of isotopes among the equivalent hydrogen atoms, the relative abundance of the isotopic ions follows a Poisson distribution,[5] and hence the relative intensities of the ^{1}H resonance peaks due to H_3O^+, H_2DO^+, and HD_2O^+ can be calculated to be in the ratio $(1 - F)^3$: $2F(1 - F)^2$: $F^2(1 - F)$. These calculated ratios and those deduced from integrals of the three signals, taken from single-sweep 220 MHz spectra with minimum dilution by sulphur dioxide, are compared in the Table. (The precision of the observed integrals was lower in the second case owing to the low overall concentration of protium in the system.)

Secondly, the middle one of the three signals is further split into a 1 : 1 : 1 multiplet (see Figure), consistent with the coupling of the protons with a single deuteron (J_{HD} 0·5 Hz). The similarly expected splitting of the weak HD_2O^+ signal into a 1 : 2 : 3 : 2 : 1 quintet has not so far been detected, but the shape of the peak suggests that it is an unresolved multiplet. The peak separations of *ca.* 0·055 p.p.m. and coupling constant of 0·5 Hz contrast with values of *ca.* 0·032 p.p.m.[12] and 0·9 ± 0·1 Hz[13] observed for the HOD–H_2O system in acetone solution.

Our observations show that the oxonium ion H_3O^+ is long-lived under the conditions of the present experiments and rule out any significant intervention of reaction (2). In ^{2}H magnetic resonance (at 13·81 MHz) we find that only the unresolved quadrupole-broadened signals from the acid and from oxonium ions are observable.

TABLE

		H_3O^+	H_2DO^+	HD_2O^+
Peak ratio for $F = 0{\cdot}250$	calc.	(1·00)	0·67	0·11
	obs.	(1·00)	0·66	0·09
Peak ratio for $F = 0{\cdot}773$	calc.	0·06	0·50	(1·00)
	obs.	0·02	0·8	(1·00)

The appearance of the ^{1}H n.m.r. spectra is essentially the same in SO_2 and in SO_2ClF, although the chemical shift of the signals depends on the diluent, since, in the condensed phase, there is inevitably some interaction between the oxonium ions and other species. In the absence of diluents the splitting of the oxonium resonance into separate signals due to the three isotopic ions is still apparent but is not complete. The difference probably results not from an essential change in the nature of the cations but from the higher viscosity of the undiluted solutions (due to the presence of anions of high molecular weight).[11]

Although the oxonium ion is long-lived in the 'super-acid' media, it would nevertheless appear to be de-stabilised relative to the hydrated oxonium ion present in aqueous solution. This is likely to be the chief factor responsible for the change in the equilibrium position of reaction (3)

$$H_3O^+ + CO_2 \rightleftharpoons (HO)_3C^+ \qquad (3)$$

on going from the solvent water [in which there is no evidence for the $(HO)_3C^+$ cation] to HSO_3F–SbF_5 [in which $(HO)_3C^+$ is a stable species].[14]

Quantitative kinetic and equlibrium studies on these systems are in progress.

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