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Hydrogen Bonding. III. Tetrapropylammonium Hydrogen Difluoride and the Thermal Elimination Reaction of Tetrapropylammonium Fluoride Hydrates[1]

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Results

In the course of studies of strongly hydrogen bonded water–anion species in tetraalkylammonium ion salt hydrates[2] we have prepared the lower hydrates of tetrapropylammonium fluoride. Removal of water from an aqueous solution of the fluoride at minimum temperatures with prolonged drying *in vacuo* gives successively the hexa-, tri-, and dihydrates; these substances are low-melting white solids which exist as crystalline slushes at room temperature. Additional water cannot be removed from the dihydrate without a concurrent Hofmann-type elimination reaction occurring.

Miller, Fried, and Goldwhite[3] have suggested that fluoride ion may function as a base in the Hofmann elimination from the observation that some ethylene, triethylamine, and residual acid are formed on extended drying of tetraethylammonium fluoride; this appears to be the only report[4] of fluoride ion functioning in this manner. We find that rapid heating of the tetrapropylammonium fluoride tri- or dihydrates to 140° *in vacuo* results in a smooth and quantitative conversion to propene, tripropylamine, and tetrapropylammonium hydrogen difluoride.

$$2(C_3H_7)_4N^+F^- \cdot 2H_2O \rightleftharpoons (C_3H_7)_3N + C_3H_6 + (C_3H_7)_4N^+HF_2^- + 4H_2O \quad (1)$$

The apparently anomalous generation of a strong acid and a fairly strong base from a neutral substance, that is, the formation of the hydrogen difluoride and tripropylamine instead of tripropylammonium fluoride, is not unexpected in light of our observations[5] on *p*-toluidinium fluoride, which is also thermodynamically unstable relative to the hydrogen difluoride and free amine. The formation of the strongly hydrogen bonded hydrogen difluoride anion provides the driving force to shift these equilibria.

Experimental Section

Eastman Kodak White Label 10% tetrapropylammonium hydroxide solution and Baker reagent grade 48% hydrofluoric acid were used as supplied. Fluoride was determined by precipitation as PbClF. Infrared spectra were recorded on a Beckman IR-12 using NaCl and Nujol mulls. The hydrates were handled under dry nitrogen at all times; polyethylene labware was used in all reactions.

Hydrates of Tetrapropylammonium Fluoride. A. Hexahydrate. A solution of tetrapropylammonium hydroxide (1.031 g, 5.07 mmol) in water (10 ml) was brought to pH 7.00 by addition of hydrofluoric acid. The solvent water was removed *in vacuo* with a rotary evaporator at room temperature for 28 hr. This afforded a white, low-melting (about 30°) crystalline mass containing a quantity of water (0.549 g, 30.5 mmol) corresponding to 6.01 mol of water for each mole of tetrapropylammonium fluoride.

B. Dihydrate. Additional heating of the hexahydrate sample from A *in vacuo* at 55° for 24 hr reduced the water content to 3.64 mol of water per mole of salt. The sample was then heated *in vacuo* at 80° for 1 hr to give a white, semicrystalline slush containing a quantity of water (0.190 g, 10.5 mmol) corresponding to 2.08 mol of water for each mole of tetrapropylammonium fluoride. Titration with base showed a negligible amount of residual acid.

C. Trihydrate. A solution of tetrapropylammonium fluoride (1.036 g, 5.07 mmol) in water (about 15 ml) was prepared exactly as in A. The solvent water was removed *in vacuo* with a rotary evaporator at room temperature for 24 hr, and then the resulting hexahydrate was heated *in vacuo* at 35° for 60 hr. This afforded a white, semicrystalline slush containing a quantity of water (0.273 g, 15.1 mmol) corresponding to 2.99 mol of water for each mole of tetrapropylammonium fluoride.

Elimination Reaction of Tetrapropylammonium Fluoride. A flask containing a crystalline slush of tetrapropylammonium fluoride (1.507 g, 7.329 mmol) and water (0.477 g, 26.5 mmol), which had been prepared as in B above, was connected to a Dry Ice cooled trap fitted with inlet and outlet stopcocks and a fitting to attach an infrared gas cell. The flask was heated rapidly to about 140°, at which point a vigorous decomposition set in. In a few minutes the slush had changed to a hard, white, crystalline mass, with obvious evolution of gas. The flask was found to contain a 99.0% yield of tetrapropylammonium hydrogen difluoride (0.819 g, 3.63 mmol) as white microcrystals. *Anal.* Calcd fo $C_{12}H_{29}NF_2$: F^-, 16.88; HF, 8.88. Found: F^-, 17.08; HF, 9.10.

The trap was removed from the system and allowed to warm in an ice bath to 0° with the stopcocks closed; it was then opened to an infrared gas cell. The vapor was shown to consist solely of propene, identified by its characteristic infrared spectrum. The trap also contained a mixture of two immiscible liquids with the odor of amine; this strongly basic mixture was rinsed from the trap with water; titration with standard hydrochloric acid showed an 88.75% yield of tripropylamine (0.467 g, 3.253 mmol). In a similar experiment the amine was separated from the water in the trap by use of a fine dropper, and identified by its nmr spectrum: δ ($CHCl_3$) triplet, 2.42, 2.30, 2.18 (area 2); sextuplet 1.75–1.05 (area 2); triplet 0.93, 0.83, 0.72 (area 3).

Identification of the Decomposing Species. A sample of tetrapropylammonium fluoride trihydrate (1.309 g, 5.07 mmol) was connected to the vacuum system with a Dry Ice cooled trap and heated *in vacuo* at 42° for 50 hr. After this time the flask contained 1.127 g of a crystalline slush; the infrared spectrum of this material showed, in addition to cation bands, the characteristic infrared spectra of the dihydrate and the hydrogen difluoride (see Discussion). Titration of the solid with sodium hydroxide showed it to contain a 17.3% yield of tetrapropylammonium hydrogen difluoride (0.098 g, 0.438 mmol).[6] Titration of the amine from the trap showed a 16.5% recovery of tripropylamine (0.60 g, 0.418 mmol). If we assume that the quantity of hydrogen difluoride represents one-half of the tetrapropylammonium ions involved in the decomposition reaction (eq 1) the sample now contains 82.7% of the original cations as tetrapropylammonium fluoride (0.857 g, 4.195 mmol) and by difference a quantity of water (0.172 g, 9.6 mmol) corresponding to 2.2 mol of water per mole of fluoride salt.

Discussion

The hydrates of tetrapropylammonium fluoride are extremely stable species, even though they are not highly crystalline at room temperature. Although specific measurements were not carried out, the behavior of the materials on drying suggests that only the hexahydrate might have a vapor pressure of water high enough to measure by manometric means at a temperature where the material was crystalline. The formation of strongly bound anion–molecule complexes without concurrent lattice stability has been observed before with the larger tetraalkylammonium ions; thus we found[7] that tetrapropyl- and tetrabutylammonium hydrogen dibromides are extremely tightly bound stoichiometric salts which are liquids at or just above room temperature.

The solid state infrared spectrum of the hexahydrate is typical of those of the clathrate hydrates[2] such as tetramethylammonium hydroxide pentahydrate[8a,9] or fluoride tetrahydrate,[8b,9] and shows, in addition to cation bands, a broad stretching band of hydrogen-bonded water centered at 3300 cm^{-1} and a bending band at 1650 cm^{-1}; no rocking modes of strongly coordinated water are present. The infrared spectrum of the tetrapropylammonium fluoride dihydrate, on the other hand, shows a stretching region for unusually strongly hydrogen-bonded water centered at 2900 cm^{-1}, a bending band at 1630 cm^{-1} which is now nearly as intense as the stretching band, and a broad, strong rocking band stretching from 600 to 1100 cm^{-1}[9]. Thus this dihydrate, like tetramethylammonium fluoride monohydrate and hydroxide monohydrate,[2,9] contains a water–anion moiety in which the water oxygen is apparently tricoordinate and involved in very strong hydrogen bonds.

The symmetrical hydrogen difluoride anion in potassium hydrogen difluoride shows ν_3 (asymmetric stretch) as a broad band at 1450 cm^{-1} and ν_2 (bending) as a fairly sharp single band at 1222 cm^{-1}.[10] The ν_1 (symmetic stretch) mode is not observed under $D_{\infty h}$ symmetry. We have reported [5]that the hydrogen difluoride anion in p-toluidinium hydrogen difluoride, which is known[11] to be a linear, unsymmetrical species of $C_{\infty v}$ symmetry, shows ν_3 as a very broad, strong band centered at 1740 cm^{-1}, and ν_2 appears as a pair of bands at 1080 and 1230 cm^{-1} as a result of the lifting of the degeneracy of this band in the asymmetric crystal environment. Subsequently we have found that ν_1 can be observed in this salt, as predicted by theory, as a broad and reasonably intense band centered at 450 cm^{-1}; there is no absorption in this area in the infrared spectrum of p-toluidinium hexachlorostannate.

In tetrapropylammonium hydrogen difluoride ν_3 (1900 cm^{-1}) and ν_2 (1255 and 1315 cm^{-1}) resemble the corresponding bands in the p-toluidinium salt; however, ν_1 does not appear in the spectrum. The ion thus is presumably still of $D_{\infty h}$ symmetry, since in either $C_{\infty v}$ or C_{2v} ν_1 would be infrared active; however, it lies in a crystal site that lifts the degeneracy of the $\Pi_u\nu_2$ bending mode. Low-temperature infrared studies of this and related hydrogen difluorides are under investigation.

Dehydration of solutions of tetramethylammonium fluoride in water yields a monohydrate; further removal of water can be effected by heating *in vacuo* at 140°.[12] Preparation of the anhydrous fluoride by this method is always accompanied by some decomposition to trimethylamine and methyl fluoride, and the decomposition is complete at higher temperatures.[13] With tetrapropylammonium fluoride it is clear that either there is no monohydrate, or it decomposes at the temperature necessary to remove water from the dihydrate to form it. The solid material which remains after the elimination reaction has been run partially to completion gives an infrared spectrum which is the composite of those of the dihydrate and the hydrogen difluoride, with no new absorptions attributable to a monohydrate, and the matter balance of the reaction shows that there are essentially 2 mol of water remaining for each mole of fluoride salt. Whether proton abstraction by fluoride occurs within the lattice of the dihydrate or in the anhydrous salt left after water is removed cannot be established at this time.

The elimination reaction of quaternary ammonium fluorides would at first appear to have limited synthetic application when compared to that of the hydroxides, since one-half of the starting amine salt is retained as the hydrogen difluoride.[14,15] However, since the fluoride salts could be prepared in neutral solution, such as by reaction of sulfates with barium fluoride or halides with silver fluoride, this process affords a means to achieve, if desirable, the results of a Hofmann elimination reaction without the need to expose a molecule to solution in aqueous base.

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Registry No.—Tetrapropylammonium fluoride hexahydrate, 51934-09-9; tetrapropylammonium fluoride dihydrate, 51934-10-2; tetrapropylammonium fluoride trihydrate, 51934-11-3; tetrapropylammonium fluoride, 7217-93-8; tetrapropylammonium hydrogen difluoride, 52003-47-1.

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On the Products of Hydroboration of 1-Chloronorbornene

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For the penultimate step in a synthesis of 1-deuterio-*exo*-norborneol, we repeated a procedure by Fry and Farn-