

stepwise ΔS° and ΔH° values for the second Zn(II)-halide complexation step ($\text{ZnX}^+ \rightarrow \text{ZnX}_2$) suggests a switch from octahedral to tetrahedral symmetry at this step, as compared to the third complexation step for Cd(II)-halide complexes.³⁰ Raman studies of Zn(II)-bromide complexes²³ indicate a very unsymmetrical bent structure (C_{2v}) for ZnBr_2 , where the role of water is not specified. The structure of ZnBr_3^- has been suggested as pyramidal,²³ C_{3v} , and as a trigonal bipyramid³⁰ with water molecules occupying the apices. Thus, the overall general shielding order for Zn(II)-halide complexes may be described as octahedral (Zn^{2+}) > approximately octahedral (ZnX^+) > trigonal bipyramidal > (ZnX_3^-) > tetrahedral (ZnX_4^{2-}) > C_{2v} (ZnX_2). Although the assignment of such definitive structures to the various Zn(II)-halide complexes is not rigorous, it is clear that, as with Cd(II), the octahedral Zn(II)-halide species are more shielded than the tetrahedral species.

Conclusion

The availability of "benchmark" chemical shift data on solids is highly useful in the interpretation of chemical shift results for liquid solutions. Using ^{113}Cd data on solid CdX_4^{2-} systems greatly enhances the reliability of the least-squares analysis of the weighted-average data on Cd(II)-halide complexes. Analogous use of solid-state chemical shift benchmarks for interpreting liquid solution data should see greatly increased popularity, e.g., for studies of organometallic species.

Acknowledgment. The authors gratefully acknowledge grants from the National Science Foundation for purchase of the NMR equipment and for support of the research under Grant CHE 74-23980.

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Trifluoromethanol (CF_3OH) and Trifluoromethylamine (CF_3NH_2)

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Abstract: Synthesis and properties of CF_3OH and CF_3NH_2 are described. Both are made from the corresponding chloro compounds CF_3OCl and CF_3NCl_2 , respectively, by reaction with HCl. Both are unstable at room temperature because of elimination of HF. While CF_3OH is a typical protonic acid, CF_3NH_2 is a base, in spite of the inductive effect of the CF_3 group.

In general hydrogen can be formally substituted by fluorine in organic compounds. Thus a huge number of compounds of that type are known or are capable of existence. But if a partly or fully fluorinated organic material contains acidic hydrogen the β position, HF elimination is observed and is responsible for difficulty in synthesizing α -fluoro alcohols.²⁻⁶ Only $\text{c-C}_4\text{F}_7\text{OH}$ is stable and well characterized;⁷ the reason for this will be discussed later.

Fluoromethanol (CF_2FOH) was claimed several times, although never isolated or characterized,^{8,9} but the protonated form has been reported¹⁰ recently.

Here we describe the preparation and characterization of

CF_3OH , the first fully fluorinated primary alcohol, which because of its acidity could also be named trifluoroorthocarbonic acid.

As with the alcohols, perfluorinated primary amines $\text{R}_F\text{CF}_2\text{NH}_2$ were also unknown hitherto. Yet CF_3NH_2 can be prepared in the same manner as CF_3OH . Some of these results have been presented in short communications.^{11,12}

Experimental Section

General. ^1H and ^{19}F NMR spectra were recorded on a JEOL 60 HL and ^{13}C spectra on a Bruker 90-MHz instrument. For Raman spectra, a Corderc PH1 with He-Ne laser excitation (190 W), for IR spectra,

a Perkin-Elmer 283, and for mass spectra, a Varian MAT CH7, were used.

Reagents. Chlorine monofluoride was prepared from equimolar amounts of ClF_3 (Matheson Co.) and chlorine in a 300-mL Monel pressure vessel at 300°C .¹³

Carbonyl difluoride¹⁴ was prepared from COCl_2 and NaF in acetonitrile at 70°C and redistilled twice in a glass vacuum line from -100 to -196°C .

Trifluoromethyl Hypochlorite.^{15,16} On an excess of thoroughly dried powdered cesium fluoride in a 100-mL stainless steel vessel 100 mmol of COF_2 and 100 mmol of ClF were condensed. The mixture was kept for 10 h at -78°C and was shaken occasionally. Then it may be warmed up to room temperature. Traces of COF_2 and ClF can be pumped off at -150°C . The CF_3OCl can be stored above the CsF in the reaction vessel. The yield was almost quantitative.

Trifluoromethyliminosulfur difluoride ($\text{CF}_3\text{N}=\text{SF}_2$) was made from cyanogen bromide and sulfur tetrafluoride, as previously described.¹⁷

Trifluoromethylamine dichloride (CF_3NCl_2) was made from CF_3NSF_2 and ClF according to ref 18.

Trifluoromethanol. CF_3OCl (10 g) was condensed into a glass or quartz trap, and CF_3Cl (50 mL) was distilled onto it. At -100°C , the mixture was homogenized by shaking and subsequently again HCl (2 g) was condensed on the mixture at -196°C . On slow warming to -100°C a rapid reaction ensued with evolution of chlorine. HCl (2 g) was again condensed on the mixture at -196°C and warming to -100°C was repeated. On cooling to -130°C CF_3OH crystallized in long needles. CF_3Cl and excess HCl were pumped off at -130°C ; the chlorine was pumped away at -110°C . In order to obtain a colorless product (free of chlorine), it is essential that this chlorine removal be done over many hours. As CF_3OH is somewhat volatile at -110°C , some is lost in this process. CF_3OH melts without decomposition at -82°C and has a vapor pressure of ca. 15 mbar at -78°C , and the boiling point is roughly estimated to be -20°C . Decomposition at higher temperatures prevented precise characterization in the gas phase. The vibrational spectra are as follows: IR (gas, -78°C) 3675 m; PQR νOH 1401 m, 1364 m, 1283 vs, 1187 s, 1117 s cm^{-1} ; Raman (solid, -140°C) 3630 w, 1455 w, 1392 m, 1370 m, 1325 w, 1285 m, 905 vs, 635 s, 440 s cm^{-1} . NMR spectra gave ^1H NMR δ 8.85 ppm (Me_4Si); ^{19}F NMR δ 54.4 ppm (CFCl_3); ^{13}C NMR quartet, δ +118 ppm (Me_4Si), $J_{\text{C-F}} = 256$ Hz. A mass spectrum showed m/e 86 (CF_3OH^+), 69 (CF_3^+), 67 (CF_2OH^+), 66 (CF_2O^+), 50 (CF_2^+), 47 (COF^+), 31 (CF^+), 28 (CO^+), 20 (HF^+), 19 (F^+).

At room temperature CF_3OH decomposes rapidly to CF_2O and HF .

Attempt to Prepare $\text{NH}_4^+\text{OCF}_3^-$. Ammonia was condensed on a solution of CF_3OH in CH_2Cl_2 at -60°C . A white solid formed immediately and dissolved partly in excess NH_3 . Unfortunately no definite stoichiometry was established for the solid product.

Trimethylammonium Trifluoroorthocarbonate [$(\text{CH}_3)_3\text{NH}^+\text{COF}_3^-$]. A solution of CF_3OH (4.8 g) in CH_3Cl (20 mL) was held at -100°C and $(\text{CH}_3)_3\text{N}$ (3.4 g) was condensed on it. At -50°C a rapid reaction gave a colorless precipitate. After several hours all volatiles were pumped off at -50°C , leaving behind a white powder. This decomposed at room temperature. Mass spectrum at -50°C : m/e 66 (COF_2^+ , 71%), 59 [$(\text{CH}_3)_3\text{N}^+$, 1.4%], 58 [$(\text{CH}_3)_2\text{CH}_2\text{N}^+$, 3%], 50 (CF_2^+ , 4%), 47 (COF^+ , 100%), 44 [$(\text{CH}_3)_2\text{N}^+$, 1%], 28 (CO^+ , 11%). These findings indicate that the material decomposes into $(\text{CH}_3)_3\text{N}$, COF_2 , and probably HF . ^1H NMR in CH_3CN (-20°C): δ_{CH} 3.3 ppm, δ_{NH} 13.5 ppm. ^{19}F NMR in CH_3CN (-20°C): δ +47.9 ppm.

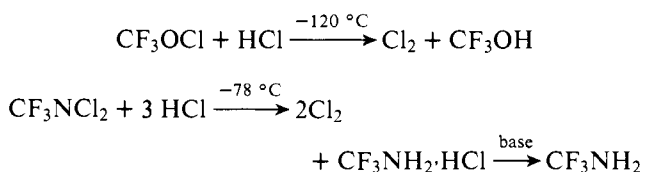
Trifluoromethylamine Hydrochloride. CF_3NCl_2 (10 g) was condensed into a glass or quartz trap and CF_2Cl_2 (20 g) was distilled on it. After homogenization of the solution a large excess of hydrogen chloride (10 g) was added at -196°C . Warming slowly to -78°C resulted in a slow reaction, forming a colorless precipitate. The reaction is much slower than in the case of CF_3OCl . After several hours at -78°C the solvent, Cl_2 and excess HCl were pumped off, yield 7.8 g (98%) of the hydrochloride. Raman (-140°C): 1647 m, 1372 m, 1315 m, 1272 m, 914 m, 869 s, 829 s, 652 w, 576 s, 436 m, 413 s, 204 vs, 184 s cm^{-1} .

Trifluoromethylamine. Trimethylamine (ca. 20 g) was condensed on the hydrochloride and the mixture was warmed to -30°C . All volatiles were pumped to another trap, leaving behind trimethylammonium chloride. The solution of CF_3NH_2 in $(\text{CH}_3)_3\text{N}$ was used for the NMR spectra: ^1H NMR: quartet at δ 6.73, $J_{\text{HF}} = 10.6$ Hz. ^{19}F

NMR: triplet at δ 48.9 ppm, $J_{\text{HF}} = 10.4$ Hz. The trimethylamine was pumped off at -78°C , leaving behind a small amount of almost pure CF_3NH_2 , mp -21°C dec. Infrared and mass spectra were taken from a sample obtained from the hydrochloride with quinoline. At room temperature the vapor of this mixture was found to be CF_3NH_2 only: IR 3484 m (νNH_2), 3407 m (νNH_2), 1611 s (δNH_2), 1310 vs, 1106 vs, 1038 s, 880 m, 722 s cm^{-1} . The mass spectrum showed m/e 85 (CF_3NH_2^+ , 85%), 69 (CF_3^+ , 62%), 66 (CF_2NH_2^+ , 95%), 65 (CF_2NH^+ , 24%), 46 (FCNH^+ , 100%) Metastable peaks at 51.4 (calcd 51.2) and 32.4 (calcd 32.1) arise from the decompositions $\text{CF}_3\text{NH}_2 \rightarrow \text{CF}_2\text{NH}_2 + \text{F}$ and $\text{CF}_2\text{NH}_2 \rightarrow \text{CFN} + \text{HF}$, respectively. Decomposition of CF_3NH_2 in the IR gas cell gives $\text{FC}\equiv\text{N}$ and HF . Solid $\text{CF}_3\text{NH}_2\cdot\text{HCl}$ decomposes to a mixture of compounds that have the composition of $(\text{FCN})_3(\text{CF}_2\text{NH})_3$ (m/e 330) or $(\text{FCN})_3(\text{CF}_2\text{NH})_2$ (m/e 265) according to their mass spectra.

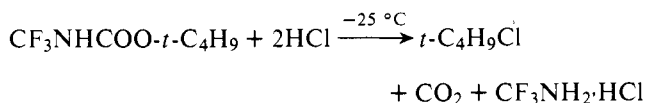
Results

Both trifluoromethanol and trifluoromethylamine are readily prepared according to eq 1 and 2. The success of these synthetic approaches appears to depend upon reaction of positive chlorine (in CF_3OCl and $\text{R}_\text{F}\text{NCl}_2$) with somewhat negative chlorine (in HCl) to form molecular chlorine and seems to be general. It was used, too, to generate HOSF_5 from ClOSF_5 .^{19,20}



Both CF_3OH and CF_3NH_2 are thermodynamically unstable toward loss of HF , but have sufficient kinetic stability to permit their manipulation below room temperature. The NMR spectra (see Figures 1 and 2) confirm the molecular formulas. The CF_3 group in CF_3OH is established by the ^{13}C NMR spectrum. The OH group is readily apparent from the gas-phase IR spectrum. The mass spectrum establishes the molecular ion. The NMR spectrum of CF_3NH_2 in $(\text{CH}_3)_3\text{N}$ (a solvent to suppress any proton migration) shows an NH_2 group and a CF_3 group with H-F splitting. The gas-phase IR shows the two characteristic lines of the NH_2 group, and the mass spectrum shows the molecular ion.

Both compounds melt sharply but decomposition prevents precise boiling point evaluation. CF_3OH is of surprisingly high volatility, but CF_3NH_2 is less volatile than anticipated. In a codistillation with triethylamine it proved to be slightly more volatile than the latter, from which a boiling point of roughly 50°C is estimated. This is far above its decomposition temperature and the boiling point of CH_3NH_2 . The acidic character of CF_3OH is evident from the reaction with bases like $(\text{CH}_3)_3\text{N}$. Salt formation with ammonia is indicated, although the product was not characterized. This acidic behavior was to be expected since the salts like K^+OCF_3^- (Rb^+ , Cs^+) are known.^{21,22} The basic character of CF_3NH_2 is lower than the basicity of normal organic nitrogen bases like $(\text{C}_2\text{H}_5)_3\text{N}$, $(\text{CH}_3)_3\text{N}$, and quinoline, as CF_3NH_2 is liberated easily from its hydrochloride with an excess of these bases. Higher substituted perfluoroamines like $(\text{CF}_3)_2\text{NH}$ and $(\text{CF}_3)_3\text{N}$ are known to be very weak bases.^{23,24} CF_3NH_2 has also been derived independently by others,¹² by cleavage of $\text{CF}_3\text{-NHCOO-}t\text{-C}_4\text{H}_9$ with HCl :



Discussion

The instability of both CF_3OH and CF_3NH_2 can be attributed to the extraordinary stability of the HF molecule and

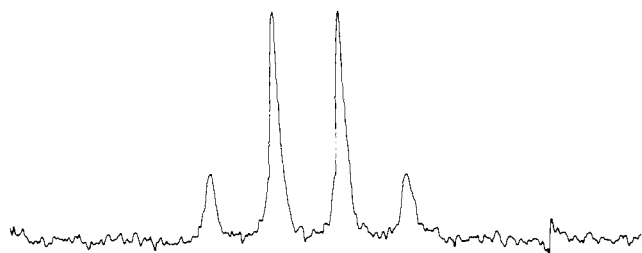


Figure 1. ^{13}C NMR spectrum of CF_3OH , -70°C , pure compound.

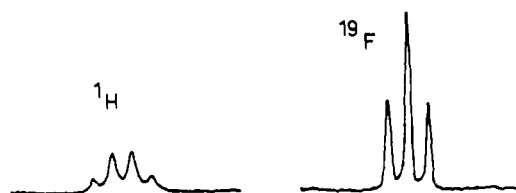


Figure 2. ^1H and ^{19}F NMR spectrum of CF_3NH_2 , -20°C , $(\text{CH}_3)_3\text{N}$ solution.

the considerable strength of the $\text{C}=\text{O}$ and $\text{C}=\text{N}$ double bonds. An estimation of the ΔH for the decomposition reaction $\text{CF}_3\text{OH} \rightarrow \text{CF}_2\text{O} + \text{HF}$ by using average bond energies for $\text{C}-\text{F}$, $\text{C}-\text{O}$, $\text{C}=\text{O}$, and $\text{O}-\text{H}$ bonds gives a value of -20 to -40 kcal/mol. But neither CF_3OH nor CF_3NH_2 is observed to be explosive. These features will be important for all primary and secondary perfluoro alcohols and should result in all being thermodynamically unstable. Tertiary alcohols such as $(\text{CF}_3)_3\text{COH}$ do not fall into this category, as β -elimination of HF is not possible. It is of interest that $c\text{-C}_4\text{F}_7\text{OH}$ is formed via HF addition to $c\text{-(CF}_2)_3\text{C}=\text{O}$.⁷ Here the poorer $\text{C}-\text{C}$ bonding energy, associated with the small (strained) ring, is an adverse thermodynamic feature of the carbonyl compound.

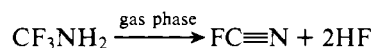
These considerations probably hold for the perfluorinated amines as well. The mechanism of the HF elimination is of special interest. The instability of both compounds limited the possibilities of following these processes adequately, so only tentative conclusions can be drawn.

In the condensed phase both species decompose in the temperature range of -30 to 0°C with a strongly increasing rate at higher temperatures. On the other hand, in the dilute gas phase (e.g., 15 mbar) IR spectra can be recorded, and the half-life at room temperature is at least 5 min under these conditions. From this we conclude that the quick HF elimination in the condensed phase is probably not an intramolecular process but rather an intermolecular one. The kinetic stability of CF_3OH and CF_3NH_2 appears to rest on unimolecular HF eliminations being forbidden on orbital symmetry grounds. It is not certain that such an elimination is forbidden for HOSF_5 . This molecule is more labile than CF_3OH (decomposing slowly at -60°C to SOF_4 and HF ²⁰), although the thermodynamics appear to be less favorable for this decomposition: a synchronous HF elimination may occur here as a consequence of higher orbital mixing in the bonding of HOSF_5 .

CF_3OH is certainly not a typical alcohol but rather an acid and can be compared with HOSF_5 , HOSeF_5 , and HOTeF_5 .²⁰ The latter two are very stable, strong acids and turned out to generate ligands $-\text{OSeF}_5$ and $-\text{OTeF}_5$ that seem to be more electronegative than fluorine.²⁶ Unfortunately the chemistry of CF_3OH (and HOSF_5) is so much more limited. Only with

extreme electronegative atoms instead of hydrogen is the elimination suppressed; FOCF_3 ,^{25,27} (FOSF_5) ,²⁸ ClOCF_3 ,^{15,16} (ClOSF_5) ,^{15,29} CF_3OOCF_3 ,³⁰ $(\text{SF}_5\text{OOSF}_5)$,³¹ and others. Salts of the OCF_3 ion^{21,22} appear to be stable with large cations.

The same comparison may hold for CF_3NH_2 as well. NH_2SF_5 is known to be a weak base^{33,34} and loses HF :



Yet the stable H_2NTeF_5 (H_2NSeF_5 is not known so far) is even less basic,³⁵ and some acidic character has been observed. This may be interpreted as higher orbital participation in H_2NSF_5 and especially H_2NTeF_5 in contrast to CF_3NH_2 . In CF_3NH_2 the relatively low basicity compared with CH_3NH_2 is clearly a result of the inductive effect to the three fluorine atoms alone.

Conclusion

The method of allowing an $-\text{OCl}$ or an $-\text{NCl}_2$ group to react with HCl at very low temperatures to give the corresponding unstable $-\text{OH}$ and $-\text{NH}_2$ compounds may be of general value. Homologue compounds with higher branched perfluoroalkyl groups should be preparable, if the chloro compound precursors can be made.

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