

Received: April 28, 1989; accepted: June 28, 1989

REACTION OF THE FLUORIDE ANION WITH ACETONITRILE, CHLOROFORM AND METHYLENE CHLORIDE

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SUMMARY

^{19}F and ^1H NMR spectra of the F^- anion in CH_3CN and CD_3CN solutions show that the F^- anion can abstract a proton from CH_3CN resulting in the slow formation of the bifluoride and acetonitrile anions. With chloroform or methylene chloride the F^- anion undergoes halogen exchange reactions at room temperature. These reactions demonstrate the exceptional reactivity of the free fluoride anion when present as a highly soluble salt.

INTRODUCTION

During recent work in our laboratory on the synthesis and characterization of anhydrous, HF_2^- free tetramethylammonium fluoride, we have used a combination of Karl Fischer titration and infrared and NMR spectroscopy to check for water and HF_2^- impurities. It was found that samples of $[\text{N}(\text{CH}_3)_4]\text{F}$, which based on their infrared spectra were free of H_2O and HF_2^- , showed significant amounts of HF_2^- in the NMR spectra of their CH_3CN solutions. The fact that the concentration of HF_2^- increased with increasing time, suggested that the HF_2^- might be generated by attack on the solvent by F^- . Since CH_3CN is frequently used as a solvent in fluorine chemistry, it is important to know whether CH_3CN undergoes a reaction with the F^- anion. Furthermore, it was interesting to examine whether polar, chlorinated hydrocarbons such as CHCl_3 or CH_2Cl_2 could be used as inert solvents for $[\text{N}(\text{CH}_3)_4]\text{F}$.

EXPERIMENTAL

The synthesis of anhydrous, HF_2^- free $[\text{N}(\text{CH}_3)_4]\text{F}$ will be described elsewhere [1]. The CH_3CN (Baker, Bio-analyzed, having an H_2O content of 40 ppm) was treated with P_2O_5

and freshly distilled in a flamed out Pyrex vacuum system prior to use, thereby reducing its water content to ≤ 4 ppm. The CD_3CN (99.96%D, Stohler) was used as received and showed only a trace of CHD_2CN as the only impurity detectable by NMR spectroscopy. The CH_2Cl_2 and the CHCl_3 (J.T. Baker, Analyzed) were dried by storage over Linde 4A molecular sieves. The CHCl_3 contained 1% of $\text{CH}_3\text{CH}_2\text{OH}$ as a stabilizer and had a water content of 0.006% before treatment with the molecular sieves. The NMR spectra were recorded on a Varian EM 390 spectrometer operating at 90 MHz for ^1H and 84.6 MHz for ^{19}F . Tetramethylsilane or CFCl_3 was used as an external standard with negative shifts being upfield from the standard. Teflon-FEP sample tubes (Wilma Glass Co.) were used for the CH_3CN reactions and glass tubes for the experiments involving CHCl_3 or CH_2Cl_2 .

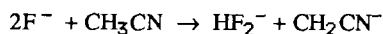
RESULTS AND DISCUSSION

Samples of $[\text{N}(\text{CH}_3)_4]\text{F}$, which based on their infrared spectra and Karl Fischer titrations were HF_2^- free and had less than 0.06 weight percent water, were dissolved in either CH_3CN or CD_3CN . Their saturated solutions in Teflon-FEP tubes were periodically monitored by ^{19}F and ^1H NMR spectroscopy for their HF_2^- content.

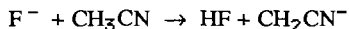
The ^{19}F NMR spectra of $[\text{N}(\text{CH}_3)_4]\text{F}$ in CH_3CN showed two signals: one intense singlet at δ -74 to -79 for F^- [2], and a doublet at δ -145 to -148 with $J_{1\text{H}19\text{F}} = 121$ Hz for HF_2^- [2, 3]. In fresh solutions, the HF_2^- concentrations were very low but increased in the course of several hours to the 5 to 10 mol% range and after standing at room temperature for several days reached a level of 30 mol%. In addition to an increase in the intensity of the HF_2^- signal, the originally colorless CH_3CN solutions also developed a yellow color on standing.

The ^1H NMR spectra of the CH_3CN solutions of $[\text{N}(\text{CH}_3)_4]\text{F}$ showed, besides the CH_3CN ($\delta = 1.96$) and $[\text{N}(\text{CH}_3)_4]^+$ ($\delta = 3.1$, $J_{1\text{H}14\text{N}} = 0.6$ Hz [4]) signals, a triplet at $\delta = 16.3$ with $J_{1\text{H}19\text{F}} = 121$ Hz characteristic for HF_2^- [3] and a broad singlet at $\delta = 9.1$ characteristic for the CH_2CN^- anion [5]. The relative intensities of the HF_2^- and CH_2CN^- signals increased together with increasing time.

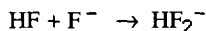
Based on the above evidence, it must be concluded that at room temperature the F^- anion was slowly reacting with CH_3CN according to:



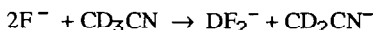
Although the NMR spectra showed no evidence for the presence of free HF, the above reaction almost certainly involves at least two steps. The first one is the slow abstraction of a proton from CH_3CN by the strong base F^-



followed by the rapid reaction of HF with the large excess of F^- present.



Conclusive proof for the generation of the HF_2^- anion from the acetonitrile solvent was obtained by substitution of the CH_3CN by CD_3CN . If the bifluoride anion is, indeed, generated from the reaction of F^- with CH_3CN , replacement of CH_3CN by CD_3CN in the reaction



should result in the following spectroscopic changes: the ^{19}F NMR spectrum should show a triplet at δ -147 with $J_{\text{D}^{19}\text{F}} = 18$ Hz for DF_2^- [6] instead of the HF_2^- doublet, and the ^1H spectrum should show no new resonances since only deuterated species are being formed. These predictions were experimentally confirmed (the only new signal was a triplet at δ -147 with a coupling constant of 17.6 Hz), and no evidence for the formation of either HF_2^- or CH_2CN^- was detected in the CD_3CN experiment. If some bifluoride had been present in the $[\text{N}(\text{CH}_3)_4]\text{F}$ starting material, it could have only been in the form of HF_2^- and, therefore, both an HF_2^- and a DF_2^- signal should have been observed since HF_2^- and DF_2^- do not undergo a fast exchange in CH_3CN [6].

The possibility of using either methylene chloride or chloroform as a solvent for $[\text{N}(\text{CH}_3)_4]\text{F}$ was also examined. It was found that at room temperature both solvents undergo a halogen exchange reaction with $[\text{N}(\text{CH}_3)_4]\text{F}$. Whereas the reaction with CH_2Cl_2 is relatively slow and CH_2ClF is the main reaction product, the reaction with CHCl_3 is quite fast and all three possible exchange products, CHCl_2F , CHClF_2 , and CHF_3 in a mol ratio of about 2:3:1 were observed by NMR spectroscopy. Thus, the ^{19}F and ^1H NMR spectra of a saturated CH_2Cl_2 solution containing some undissolved $[\text{N}(\text{CH}_3)_4]\text{F}$ exhibited, in addition to intense signals due to the free fluoride anion (singlet at δ -97.0 with a line width of 3 Hz) and the $[\text{N}(\text{CH}_3)_4]^+$ cation (singlet at δ 3.44), a triplet at δ -169.4 and a doublet at δ 5.93 with $J_{\text{HF}} = 49$ Hz which are characteristic for CH_2ClF [7]. For a saturated CHCl_3 solution containing some undissolved $[\text{N}(\text{CH}_3)_4]\text{F}$, the F^- anion signal at δ -120.3 was weak and disappeared quickly giving rise to doublets at δ -78.3 with $J_{\text{HF}} = 79.1$ Hz, δ -80.8 with $J_{\text{HF}} = 54.3$ Hz, and δ -84.3 with $J_{\text{HF}} = 75.0$ Hz, which are characteristic for CHF_3 [8], CHCl_2F [9, 10], and CHClF_2 , respectively. Although halogen exchange reactions involving chlorinated

hydrocarbons and ionic fluorides are well known [11, 12], the mild conditions under which the above described reactions proceed are surprising.

CONCLUSION

Although CH_3CN is an excellent solvent for $[\text{N}(\text{CH}_3)_4]\text{F}$, it is not chemically inert. The strongly basic F^- anion can abstract a proton from CH_3CN with the formation of the HF_2^- and CH_2CN^- anions. Similarly, CHCl_3 and CH_2Cl_2 readily react with $[\text{N}(\text{CH}_3)_4]\text{F}$ at room temperature undergoing halogen exchange reactions thus demonstrating the high reactivity of the free fluoride anion.

ACKNOWLEDGMENT

The authors are grateful to the Office of Naval Research and the Army Research Office for financial support and to Dr. C. J. Schack and Mr. R. D. Wilson for their help.

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