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

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## SUMMARY

$^{19}$F and $^1$H 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 $[N(CH_3)_4]F$, 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 $[N(CH_3)_4]F$.

## EXPERIMENTAL

The synthesis of anhydrous, $HF_2^-$ free $[N(CH_3)_4]F$ will be described elsewhere [1]. The $CH_3CN$ (Baker, Bio-analyzed, having an $H_2O$ content of 40 ppm) was treated with $P_2O_5$

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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 $CH_3CH_2OH$ 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 (Wilmad 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 $[N(CH_3)_4]F$, 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 $[N(CH_3)_4]F$ in $CH_3CN$ showed two signals: one intense singlet at $\phi$ -74 to -79 for $F^-$ [2], and a doublet at $\phi$ -145 to -148 with $J_{^1H^{19}F} = 121$ 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 $[N(CH_3)_4]F$ showed, besides the $CH_3CN$ ($\delta = 1.96$) and $[N(CH_3)_4]^+$($\delta = 3.1$, $J_{^1H^{14}N} = 0.6$ Hz [4]) signals, a triplet at $\delta = 16.3$ with $J_{^1H^{19}F} = 121$ 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:

$$2F^- + CH_3CN \rightarrow HF_2^- + CH_2CN^-$$

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 $F^-$

$$F^- + CH_3CN \rightarrow HF + CH_2CN^-$$

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

$$HF + F^- \rightarrow HF_2^-$$

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

$$2F^- + CD_3CN \rightarrow DF_2^- + CD_2CN^-$$

should result in the following spectroscopic changes: the $^{19}F$ NMR spectrum should show a triplet at Ø -147 with $J_{^2D^{19}F}$ = 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 Ø -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 $[N(CH_3)_4]F$ 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 $[N(CH_3)_4]F$ was also examined. It was found that at room temperature both solvents undergo a halogen exchange reaction with $[N(CH_3)_4]F$. 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 $[N(CH_3)_4]F$ exhibited, in addition to intense signals due to the free fluoride anion (singlet at Ø -97.0 with a line width of 3 Hz) and the $[N(CH_3)_4]^+$ cation (singlet at δ 3.44), a triplet at Ø -169.4 and a doublet at δ 5.93 with $J_{HF}$ = 49 Hz which are characteristic for $CH_2ClF$ [7]. For a saturated $CHCl_3$ solution containing some undissolved $[N(CH_3)_4]F$, the $F^-$ anion signal at Ø -120.3 was weak and disappeared quickly giving rise to doublets at Ø -78.3 with $J_{HF}$ = 79.1 Hz, Ø -80.8 with $J_{HF}$ = 54.3 Hz, and Ø -84.3 with $J_{HF}$ = 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 $[N(CH_3)_4]F$, 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 $[N(CH_3)_4]F$ at room temperature undergoing halogen exchange reactions thus demonstrating the high reactivity of the free fluoride anion.

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