

Widening the alkyl hypofluorite family. On the existence of ethyl hypofluorite

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Abstract

Unlike methanol and t-butanol, most other alcohols do not form alkyl hypofluorites when reacting with fluorine, since immediate HF elimination takes place even at low temperatures. Notable exceptions to this trend are the two deuterated ethanols $\text{CD}_3\text{CD}_2\text{OD}$ and $\text{CH}_3\text{CD}_2\text{OH}$, which do produce the corresponding hypofluorites. Their identification and some of the reasons for this exclusive behavior are outlined.

Keywords: Alkyl hypofluorites; Deuterated ethyl hypofluorite; NMR spectroscopy

1. Introduction

Several hypofluorites containing a perfluoroalkyl or perfluoroacyl group have been described in the literature. The first and the best known member is fluoroxytrifluoromethane, CF_3OF , synthesized by Kellogg and Cady more than 45 years ago [1], but other derivatives such as $\text{CF}_2(\text{OF})_2$ [2], $\text{CF}_3\text{CF}_2\text{OF}$ [3] and CF_3COOF [4] have also been prepared and used in chemistry. More than 10 years ago we prepared acetyl hypofluorite, CH_3COOF , the first compound in which the OF group was not attached to a polyfluorinated alkyl or acyl residue [5]. Its synthesis was evidence that the OF moiety and alkyl groups can coexist without immediate decomposition via HF elimination. Almost 10 years later we took an additional step in this direction by making methyl hypofluorite, MeOF [6], and shortly afterwards the t-butyl hypofluorite, $(\text{CH}_3)_3\text{COF}$ [7], both relatively stable. There is evidence that at least MeOF decomposes through HF elimination with formation of formaldehyde. Our goal in this work was to find if this young family of alkyl hypofluorites can be extended or if it is limited to the above two examples.

2. Results and discussion

Following the synthesis of MeOF and $t\text{-BuOF}$, the obvious continuation was to try to prepare EtOF , PrOF and similar

hypofluorites, but when we employed similar conditions (passing dilute F_2 either through the neat alcohols or through their CH_3CN or $\text{CH}_3\text{CH}_2\text{CN}$ solutions) no oxidative material was obtained, and the only result was the gradual disappearance of the corresponding alcohol and HF formation. In order to minimize the possibility of HF elimination in ethanol and propanol, we tried using 2,2,2-trifluoroethanol, $\text{CF}_3\text{CH}_2\text{OH}$, and 3,3,3,2-pentafluoropropanol, $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$, but with the same negative results as far as oxidative hypofluorite formation was concerned. Turning to isopropanol or even to 1,1,1,3,3,3-hexafluoro-2-propanol $\{(\text{CX}_3)_2\text{CHOH}$, $\text{X} = \text{H}$, $\text{F}\}$ did not help, and the single hydrogen α to the OH group proved to be an insurmountable barrier to the formation of the hypofluorite moiety or to its stability, if indeed it is initially formed.



slow decomposition; no oxidative hypofluorites

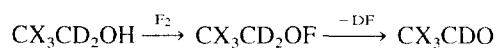
($\text{R} = \text{CF}_3$, CF_3CF_2 , CH_3 , CH_3CH_2 ; $\text{R}' = \text{H}$, $\text{R} = \text{R}' = \text{CH}_3$, CF_3)

This situation was similar to the one we faced in our study of the synthesis of various hydrogen-containing acyl hypofluorites. The conclusion from that study was that a heteroatom α to the carboxylic acid, which strengthens the geminal C–H bond, was necessary for the formation and stability of the corresponding acyl hypofluorites, RCHXCOOF ($\text{X} = \text{Cl}$, NO_2) [8]. Alcohols of similar type (RCHXOH , $\text{X} = \text{Cl}$, F , NO_2) do not normally exist, and the only other way to find

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out whether the C–H bond strength is indeed a dominant factor in alkyl hypofluorite formation was to check alcohols with deuterium atoms α to the OH moiety, since the C–D bond is usually stronger than the C–H one.

Thus we were delighted to find that reacting an acetonitrile solution of $\text{CD}_3\text{CD}_2\text{OD}$ with fluorine at -40°C formed an oxidative solution with concentrations of up to 0.05 molar. Repeating the experiment at -75°C using propionitrile as a solvent resulted in even higher oxidant concentrations up to 0.1 molar¹. However, any attempt to react this oxidant with electron-rich centers such as various types of double bonds, including enol derivatives, resulted in its immediate decomposition without affecting the organic substrate. Still, spectral evidence clearly points to the formation of the desired $\text{CD}_3\text{CD}_2\text{OF}$. The ^{19}F NMR spectrum, measured at -35°C , shows a signal at +50.5 ppm, a little higher than the corresponding resonance in $^1\text{BuOF}$: +67 ppm. The width at half-height of this signal is 20 Hz, which indicates a $^3J_{\text{FD}}$ value of about 6–7 Hz and is in good agreement with the $^3J_{\text{FH}}$ value in CH_3OF , which was found to be 45 Hz. The ^2H NMR spectrum, also taken at -35°C , shows a signal at 1.28 ppm for the CD_3 group, representing a shift of +0.08 ppm compared to the starting material. The deuterium nuclei of the CD_2OF group can be found at 4.75 ppm, an upfield shift of 1.08 ppm from the starting material, very similar to the shift caused by the fluorine atom on the methyl hydrogens in CH_3OF . When the deuterated hypofluorite is warmed to 20°C , it quickly decomposes and the oxidate power disappears along with the signals at 1.28 and 4.75 ppm. Two new peaks at 2.0 and 9.8 ppm suggest that the decomposition product is CD_3CDO , obtained via DF elimination from the hypofluorite.

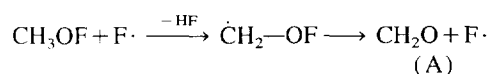
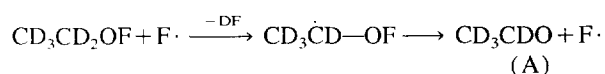
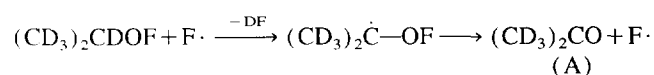


(X = H, D)

In order to show that the α hydrogens represent the most important factor as far as the stability of alkyl hypofluorites is concerned, we repeated the above set of experiments with ethyl-1,1- d_2 alcohol, $\text{CH}_3\text{CD}_2\text{OH}$. Reacting a cold (-75°C) propionitrile solution of this deuterated alcohol with fluorine resulted in an oxidative solution of up to 0.05 molar¹. As in the previous case, the ^{19}F NMR spectrum taken at -35°C shows a signal at +50.1 ppm, while the ^2H NMR spectrum shows a peak at 4.58 ppm corresponding to the CD_2OF group and representing a downfield shift of 1.07 ppm from the starting material. Similar to $\text{CD}_3\text{CD}_2\text{OF}$, this hypofluorite did not react with any olefin and tended to decompose very quickly at room temperature.

We have shown in the past that the main thermal decomposition pathway of acyl hypofluorites involves a radical chain [9]. It is reasonable to assume that this is the case with alkyl hypofluorites as well. The stability of MeOF relative to

EtOF can be attributed to the thermodynamically unfavorable pathway for the formation of the corresponding primary radical compared to the more substituted ethoxy one. This can explain also the negative results we obtained when we tried to repeat this reaction with perdeuterated 2-propanol, $(\text{CD}_3)_2\text{CDOD}$. Although all the hydrogens were replaced with deuterium nuclei the formation of the secondary radical $(\text{CD}_3)_2\text{C}(\cdot)\text{OF}$ is more favorable than $\text{CD}_3\text{CD}(\cdot)\text{OF}$, and hence the decomposition is faster even at low temperatures.



where A corresponds to decomposition products which have been detected. (Fluorine atoms can originate either from an initial decomposition of the hypofluorite or from the fluorine itself.)

In conclusion, it seems at this point that deuterated ethanol is the border line between suitable and unsuitable substrates for alkyl hypofluorite formation. This also forces us to conclude that the family of alkyl hypofluorites is indeed quite a limited one; the two most important factors for its existence are the C–H (or C–D) bond strength and how favorable is the radical chain decomposition.

3. Experimental details

^2H NMR spectra were recorded at -35°C on a Bruker ARX-500 spectrometer at 76.77 MHz with acetonitrile or propionitrile as solvents and $(\text{CD}_3)_2\text{CO}$ as either internal or external marker at 2.07 ppm. The ^{19}F NMR spectra were measured also at -35°C on a Bruker AMX-360 WB spectrometer at 338.8 MHz and are reported in parts per million (ppm) using CFCl_3 as internal standard.

3.1. General procedure for working with fluorine

Fluorine is a strong oxidant and a very corrosive material. An appropriate vacuum line made from copper or Monel in a well-ventilated area should be constructed for working with this element. Additional, more detailed experimental information on how we handle it appears elsewhere [10]. For the occasional user however, various premixed mixtures of F_2 with inert gases are commercially available, simplifying the whole process. The reactions themselves can be carried out in glass vessels. If elementary precautions are taken, work with fluorine is relatively simple, and we have had no bad experiences working with this element.

¹ The oxidant concentration was determined through reacting an aliquot with aqueous KI solution followed by iodometric titration. It was assumed that this is a two-electron oxidation, so that each mole of the oxidant generates 1 mol of iodine.

3.2. Preparation of deuterated EtOF

A mixture of 15% F₂ in N₂, with a total of about 20 mmol fluorine, was bubbled through a cold (–40 °C when working with acetonitrile as a solvent and –75 °C with propionitrile) solution of 5 ml CD₃CD₂OD in 25 ml of solvent placed in a Teflon vessel. About 0.015 or 0.03 mol of CD₃CD₂OF was obtained in CH₃CN and propionitrile, respectively. Passing more fluorine did not increase the oxidant concentration, which could be easily determined by reacting aliquots of the reaction mixture with aqueous KI and titrating the liberated iodine. A similar procedure, with similar results, was employed when CH₃CD₂OH was used as a substrate to form CH₃CD₂OF.

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