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ON THE EXISTENCE OF ACETYL HYPOFLUORITE

DAVID HEBEL , ORI LERMAN and SHLOMO ROZEN*

School of Chemistry, Tel Aviv University, Tel Aviv 69978 (Israel)

SUMMARY

^{1}H and ^{19}F NMR spectra along with GC studies of the oxidizing solution obtained from the reaction of F_2 with NaOAc , support the notion that a single compound with molecular structure CH_3COOF indeed exists.

Acetyl hypofluorite, CH_3COOF, which was first prepared in our laboratories [1] is used as an electrophilic fluorinating agent. It seems to be the mildest reagent among those possessing the fluoroxy moiety, thus turning it into a useful tool for fluorination of activated aromatic rings [2], carbonyl compounds [3] and double bonds [4]. Its convenient preparation from F_2 and its very short reaction times with various organic substrates make it a key reagent in the synthesis of ^{18}F containing molecules such as ^{18}F-2-deoxy-2-fluoro-D-glucose used for the rapidly developing Positron Emitting Transaxial Tomography - PETT. For this purpose $AcO^{18}F$ was prepared by several investigators some of them introducing their own variations to the basic reaction of F_2 with acetic acid salts

[5]. The in situ prepared acetyl hypofluorite was never isolated, nor was it properly identified, mainly because of its instability when in pure form. This might raise a question of whether this molecule really exists, or maybe it is a mixture of reagents which react eventually in a way that adds the elements of AcO and F across various bonds [6].

We wish to report here for the first time some spectral and other evidence pointing to the fact that AcOF is a real molecule. Usually, we prepare this reagent by passing 6-8% F_2 in N_2 through a cold suspension of NaOAc in $CFCl_3$ (freon) either in the presence or in the absence of AcOH [1]. Although from the synthetic point of view $CFCl_3$ is the solvent of choice, it creates difficulties, when in large excess, for FT- ^{19}F NMR measurements of dilute solutions. Attempts to replace the $CFCl_3$ with another unfluorinated solvent resulted always in decomposition of the oxidizing material. This problem was solved when we selectively surpressed the intense freon signal using the 1331 sequence [7] for the ^{19}F NMR measurements. When such a measurement was performed at -78°C for the AcOF, obtained in the absence of AcOH, the oxygen bound fluorine resonated as a slightly broad signal at +168 ppm (W h/2 =15Hz, in good agreement with $^4J_{HF}$ = 3.6Hz) a very characteristic field for a fluoroxy group [8]. Measuring the ^1H NMR spectrum of the same solution at the same low temperature reveals the methyl group of the AcOF resonating at 2.12 ppm (d, $^4J_{HF}$=3.6Hz). Very small signals could also be detected at 5.07 ppm (d, J_{HF}=46 Hz) and at 5.65 ppm (t, J_{HF}=50 Hz) originating from minor radical fluorination at the CH_3 group producing CH_2F and CHF_2 derivatives respectively [9]. Additional minor signals resonating between 2.15-2.50 ppm were also observed. These signals apparently belong to various by-products which are always formed when no acetic acid is present in the reaction mixture.

Because of the above by-products, of which some seem to be quite reactive, it is more convenient to prepare the AcOF in freon containing about 10% acetic acid, or by using NaOAc solvated with AcOH. In order to verify that the same oxidizing compound is formed in this case as well, the ^{19}F and ^{1}H NMR spectra were taken under identical conditions as above including filtration at -78°C leaving out most of the frozen AcOH. No change was found in the ^{19}F NMR although the proton spectrum was free from all the by-product's signals at 2.15-2.50 ppm. This is in accordance with the observed fact that cleaner reactions and better yields were obtained when the AcOF was produced by this method [3b,4]. A signal at 2.10 ppm belonging to AcOH could also be found in this case. The ratio of the intensity of both methyl peaks, of CH_3COOH and CH_3COOF, is about 1:1. The same ratio is also found in an independent experiment where we titrated the acid and the oxidizing CH_3COOF.Since these ratios are reproducible at various concentrations, they might support the idea that some complexation or solvation does exist between the AcOF and the polar acetic acid. As a matter of fact, we found that polar solvents such as AcOH or water stabilize the AcOF to such an extend that its solutions do not decompose for at least several hours at room temperature, which is in sharp contrast to its behaviour when polar solvents are absent.

An attempt to measure the FT-IR spectrum of AcOF was inconclusive. As with the ^{19}F NMR, the fluorinated solvent interfered with the measurements since it has very strong bands in the 1000-600 cm^{-1} region, where the O-F bond was expected to absorb [8,10]. Trying to subtract the solvent bands from the oxidizing solution resulted in a very small extra peak at 660 cm^{-1} about which we are very reluctant to draw any conclusion. It is likely that most of the AcOF decomposed during the measurement itself.

The easy decomposition of the AcOF however, helped us in another way to determine its existence. When the oxidizing solution was injected to GC at 70°C, we were able to detect only CH_3F and CO_2 in 1:1 ratio.

$CH_3CO\text{-}O\text{-}F \text{ ---> } CH_3F + CO_2$

No other oxidizing material could decompose only into these two products in such a ratio. This result is in full agreement with the parallel behaviour of CF_3COOF which similarly decomposes into CF_4 and CO_2 [11].

EXPERIMENTAL

Full description of the preparation and some of the reactions of AcOF with organic substrates can be found in ref.[1-3]. The sodium acetate used in this work was dried in vacuo for several hours and used either immediately or after treatment with 1-2 equivalents of AcOH. The NMR spectra were measured at -78°C using a Bruker WH-360 spectrometer . $CFCl_3$ and TMS served as external references for ^{19}F(at 338.8 MHz) and ^{1}H (at 360 MHz) NMR respectively. The GC experiments were performed on a machine adapted for gas measurements and equiped with a 12 foot Propak Q column and a TC detector, with helium serving as a carrier. The gases liberated by the CH_3COOF decomposition had the same retention time as authentic samples of CH_3F and CO_2 either in separate injections or when a mixture of these gases and AcOF was applied.

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