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On reactions of carbon disulphide induced by 'naked' fluoride
Part 2: Reactions with 2-*H*-heptafluoropropane, hexafluoropropene, and bis(2,2,2-trifluoroethyl)amine [1]

Stephan Rüdiger *, Konrad Seppelt

Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstraße 34-36, D-14195 Berlin, Germany

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Abstract

The reaction of CS_2 and tetramethylammonium fluoride (TMAF) with 2-*H*-heptafluoropropane (R227) leads to 2,4-bis(hexafluoroisopropylidene)-1,3-dithietane as well as to the tetramethylammonium salt of heptafluorodithioisobutyric acid. The latter anion resulted also from the reaction of CS_2 and CsF with hexafluoropropene (HFP), whereas CS_2, TMAF and HFP reacted to compounds derived from HFP dimerization. *N,N*-bis(2,2,2-trifluoroethyl)dithiocarbamic acid anion was obtained from bis(trifluoroethyl)amine reacted with CS_2 and TMAF. © 1997 Elsevier Science S.A. All rights reserved.

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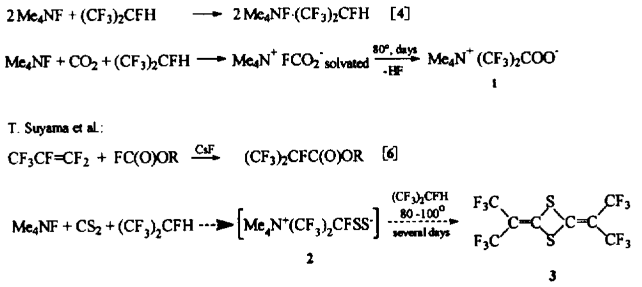
1. Introduction

The hypothetic 'naked' fluoride, which should exhibit both a very high basicity and a high nucleophilicity, can be well approximated by tetramethylammonium fluoride (TMAF) [1]. Expectedly, the strong nucleophile reacts with CS_2, yielding FCS_2^- [2]. Formation of the latter is a necessary assumption to explain nucleophilic substitution reactions with fluoroaromatics [3], whereas other reactions with CS_2/F^- could be induced by F^- acting as a strong base too. Some examples of the latter type of reaction are given in the following.

2. Results and discussion

TMAF can be dissolved in 2-*H*-heptafluoropropane (R227) from which it may be obtained as 2:1 solvate [4] (Scheme 1). Because of this solubility, the reaction of TMAF with CO_2, which is known to yield $(CH_3)_4N^+ FCO_2^-$ [5], was repeated in R227 aiming at single crystals of the fluoroformate. Expectedly, TMAF reacts immediately with CO_2 in R227 to give solvated tetramethylammonium fluoroformate.



Scheme 1.

Prolonged heating of the reaction mixture at about 80 °C over several days did not yield the single crystals but the tetramethylammonium salt of heptafluoroisobutyric acid (1) (Scheme 1). This reaction corresponds with those reported by Suyama et al. [6], who obtained esters of heptafluoroisobutyric acid by reacting hexafluoropropene (HFP) with esters of fluoroformic acid in the presence of caesium fluoride (Scheme 1).

Similar experiments with CS_2 instead of CO_2 came to unexpected results. CS_2 reacts with TMAF in R227 smoothly too, yielding immediately a solid reddish product insoluble in R227, presumably the FCS_2^- salt. When the reaction mixture was held at 70–75 °C for about 6 days, the solid became dark, deep red. After removal of unreacted R227 and CS_2 in vacuo, the residual solid was extracted with ether or acetone, and the extracts analysed. It was found that 2,4-bis(hexafluoroiso-

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* Corresponding author.

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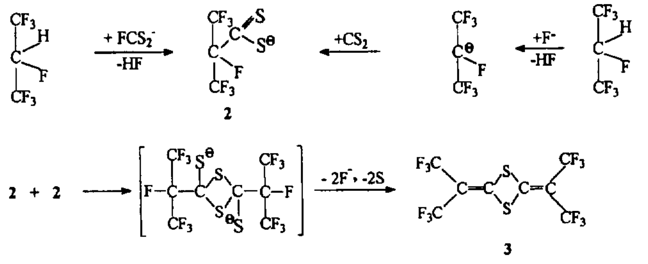


Scheme 2.

propylidene)-1,3-dithietane (**3**) had been formed (Scheme 1) together with other products not identified. The analytical data of **3** are in agreement with those reported by Raasch [7].

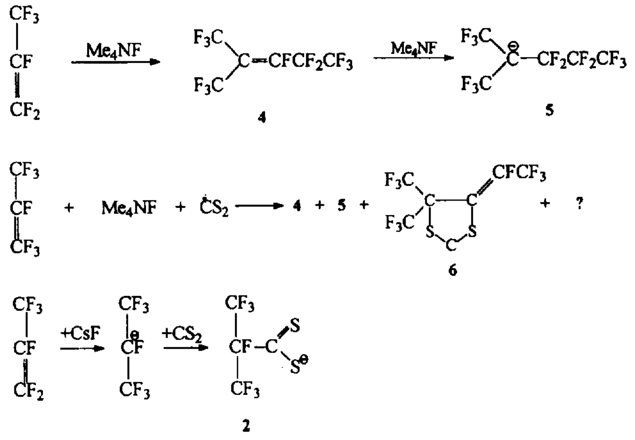
In Scheme 2, a mechanism of the formation of dithietane is proposed, which implies intermediate formation of the anion of heptafluorodithioisobutyric acid (**2**). The involvement of this is supported by its detection in separate experiments. As in the case of the reaction with CO_2, **2** (or **1** respectively) could be formed in two ways (Scheme 2). The path via dithiofluoroformate (or fluoroformate respectively) is more likely not only because of the similarity to the reaction of Suyama et al. [6], but also because it does not need the formation of substantial amounts of heptafluoropropane carbanion, which should cause HFP dimers or HFP oligomers as by-products. The latter were not detected in the reactions discussed but were always detected when TMAF was allowed to react with R227 in the presence of a polar solvent.

The situation changes with HFP being used instead of R227. TMAF reacts with HFP exothermically by dimerization of the latter, yielding nearly exclusively perfluoro(2-methyl-pentene-2) (**4**) [8] as well as its carbanion (**5**) [9] (Scheme 3). If TMAF is reacted with HFP in the presence of CS_2, the same products are predominant, however, at least two additional products are formed. One of them was tentatively assigned, based primarily on MS data, to 1,3-dithia-2-thion-4,4-bis(trifluoromethyl)-5-tetrafluoroethylidene-cyclopentane (**6**) (Scheme 3).

The same reaction was tried with CsF. On heating a mixture of HFP, CS_2 and CsF at about 80 °C for several days, the CsF became a rather voluminous pale yellow powder, which proved to be the caesium salt of heptafluorodithioisobutyric acid (Scheme 3), whilst excessive HFP and CS_2 remained unchanged.

These results show that in HFP the 'naked' fluoride ion of TMAF, the reactivity of which is much higher than that of CsF, forces the reaction primarily towards the formation of HFP carbanion and its reaction products **4**, **5**, and **6**, whereas in R227 the reactivity of TMAF is distinctly reduced to about that of CsF in HFP, obviously by solvation.

Reactions of CS_2 with secondary amines are used to prepare *N*,*N*-dialkyl-dithiocarbamic acid. Thus, diethylamine can be reacted under mild conditions, for example in the presence of aqueous NaOH; under similar conditions, bis(2,2,2-trifluoroethyl)amine (**7**) does not react. However, under the action of TMAF, **7** reacts smoothly with CS_2, yielding the expected tetramethylammonium salt of *N*,*N*-bis(2,2,2-trifluoroethyl)dithiocarbamic acid (**8**) (Scheme 4), which could be characterized by its ^{19}F NMR, ^{1}H NMR, ^{13}C NMR, IR, Raman and FAB-MS spectra. The reaction could proceed basically in two ways (Scheme 4), which differ in their respective primary attack of the 'naked' fluoride, which could be either on the amine (path (i)) or on the CS_2 (path (ii)). TMAF reacts slightly exothermically with **7**, but this is obviously solvation rather than amide formation. Thus it is likely that despite its reduced reactivity, the solvated fluoride reacts with CS_2 (path (iii)), and the dithiofluoroformate formed this way reacts immediately with the solvate **7** yielding the observed anion of *N*,*N*-bis(2,2,2-trifluoroethyl)dithiocarbamic acid (**8**).



Scheme 3.

$$\underset{7}{(CF_3CH_2)_2NH} + Me_4NF + CS_2 \longrightarrow \underset{8}{[(CF_3CH_2)_2NCSS]^- [Me_4N]^+} + HF$$

$$\text{i} \quad 7 \xrightarrow[-HF]{+F^-} [(CF_3CH_2)_2N]^- \xrightarrow{+CS_2} 8$$

$$\text{ii} \quad F^- + CS_2 \longrightarrow FCS_2^- \xrightarrow{-HF} 8$$

$$\text{iii} \quad F^- + 7 \longrightarrow F^-_{\text{solvated}} \xrightarrow{+CS_2} [FCS_2^-{}_{\text{solvated}}] \xrightarrow{-HF} 8$$

Scheme 4.

3. Experimental details

^{19}F NMR spectra were recorded with a Jeol FX90Q spectrometer at 84.25 MHz using $CFCl_3$ as external standard with upfield values designated negative. ^{1}H NMR spectra were recorded with a Jeol FX90Q spectrometer at 89.55 MHz using TMS as external standard. ^{13}C NMR spectra were recorded with a Bruker AC250 spectrometer at 62.896 MHz using TMS as external standard. IR spectra were recorded with a Perkin-Elmer 983 instrument either in KBr or in a 10 cm gas cuvette with KBr windows. Raman spectra were recorded with a Ramalog (Spex) instrument using an argon laser (488 and 514 nm). FAB-MS spectra were obtained with a Varian-Mat CH_5DF instrument using xenon, only negative ions were recorded. GC/MS was carried out with a Varian Saturn II instrument using a 50 m Norion capillary coated with NB 54 phase.

TMAF was prepared according to Christe et al. [1]. Solvents were dried applying standard procedures. Bis(2,2,2-trifluoroethyl)amine (Fluorochem Ltd.) as well as hexafluoropropene and 2-*H*-heptafluoropropane were used as supplied.

3.1. General procedure

All reactions were carried out in thoroughly dried glass tubes of ca. 8 mm external diameter, fused at one end. Whereas solid compounds were handled in a dry-box, liquid and gaseous compounds were distilled at or below room temperature against − 196 °C using a vacuum system. After all the reaction mixture components had been condensed in, the glass tubes were fused at the open end, and kept in an air oven under the conditions indicated. Then the tubes were cooled below the boiling points of the respective reactants, opened under exclusion of air, and volatiles were distilled off.

3.2. Reactions with R227

Synthesis of **1**. 90 mg (0.97 mmol) TMAF, 130 mg (2.9 mmol) CO_2 and excess R227 were reacted for several weeks at room temperature with repeated warming to 80 °C followed by slow cooling down. The reaction mixture consisted of a white solid and a liquid phase. The solid was freed from all volatiles at room temperature in oil vacuum, one part of it was dissolved in H_2O, another in diluted sulphuric acid which was subsequently extracted with ether. ^{19}F NMR spectra of the etheral solution showed signals at − 75 ppm (d, $J_{FF} = 7.3$ Hz) and at − 181 ppm (m, $J_{FF} = 7.3$ Hz), and of the aqueous solution at − 73 ppm (d, $J_{FF} = 7.5$ Hz) and at − 172 ppm (m, $J_{FF} = 7.5$ Hz) (besides signals of F^-, and SiF_6^-), corresponding to those of heptafluoroisobutyric acid and its anion (**1**) respectively. From GC/MS of the etheral solution, the MS data are in agreement with $(CF_3)_2CFCOOH$: 214 (M^+), 150 ($C_3F_6^+$), 69 (base peak), 45 ($COOH^+$).

Synthesis of **2**. 80 mg (0.86 mmol) TMAF, 450 mg (5.9 mmol) CS_2 and excess R227 were kept at 80 °C for 48 h. After that time the reaction tube was opened, volatiles distilled off (unreacted CS_2 and R227 only), and the brownish residue dissolved in water. In the ^{19}F NMR spectrum of the aqueous solution were signals at − 73 ppm and at − 173 ppm, identical with those of heptafluorodithioisobutyric acid anion (**2**) obtained on reaction of CS_2 with HFP and CsF (see later).

Synthesis of **3**. In a similar experiment, 90 mg (0.97 mmol) TMAF, excess CS_2 and excess R227 were reacted at 70–75 °C for 9 days. After that time, gas phase IR spectra of the volatiles distilled off showed at the end of the distillation the presence of an absorption band at 1618 cm^{-1}, besides the characteristic bands of CS_2 and R227. Extraction of the residual deep brown solid with ether gave a deep red solution which had in its ^{19}F NMR spectrum a strong signal at − 59 ppm, besides some smaller signals. Successive extraction with acetone yielded a brownish red solution, the ^{19}F NMR spectrum of which consisted of a strong peak at − 59.3 ppm and a much smaller peak at − 54.5 ppm. According to GC/MS, the ether solution contained basically one compound. MS: 388 ($C_8F_{12}S_2^+$, M^+, 73%), 369 ($M–F^+$), 194 ($C_4F_6S^+$, $M/2^+$, 47%), 175 ($C_4F_5S^+$, 53%), 106 ($C_3F_2S^+$, 35%), 69 (base peak). IR, ^{19}F NMR, and MS data are in accordance with those of 2,4-bis(hexafluoroisopropylidene)-1,3-dithietane (**3**) [7].

3.3. Reactions with HFP

Synthesis of **4** and **5**. Excess HFP (about 3–4 mmol) was condensed on about 1 mmol TMAF. With rising temperature, a slightly exothermic reaction started at room temperature, which was completed by keeping the mixture at about 60 °C over 24 h. The liquid phase consisted now nearly exclusively of a HFP dimer, i.e. perfluoro(2-methyl-pentene-2) (**4**), identified by its ^{19}F NMR spectrum [8], whereas TMAF was transformed into a yellow, sticky product, soluble in acetonitrile, which proved [9] to be perfluoro-2-methylpentan-2-yl(tetramethylammonium) (**5**).

Synthesis of **4**, **5** and probably **6**. 130 mg (1.4 mmol) TMAF was reacted with 144 mg (1.9 mmol) CS_2 and excess HFP at 70–80 °C for 7 days. After that time, the liquid phase consisted according to its ^{19}F NMR spectrum mainly of **4**, whereas the ^{19}F NMR spectrum of the MeCN solution of the residue was that of a rather complex mixture. Again, the major constituent was the carbanion **5**, and by fractional extraction of the solid with MeCN, two sets of ^{19}F NMR peaks were found to be likely to belong to individual compounds, i.e. at − 52, − 58, − 76 and − 100 ppm, and at − 48, − 54, − 80 and − 116 ppm respectively. GC/MS of the MeCN solution showed also several compounds present, among them were small amounts of HFP-dimer and also HFP-trimer. A major constituent had MS $(m/e)^+$ 370, 294, 275, 225, 175, 144, 87, 76, 69 (base peak), 63, and 44. These data can be tentatively assigned to 1,3-dithia-2-thio-4,4-bis(trifluoromethyl)-5-tetrafluoroethylidene-cyclopentane (**6**), MW 370, which could fit the first set of ^{19}F NMR peaks mentioned above.

Synthesis of **2** from CsF. 160 mg (1.05 mmol) CsF, 200 mg (2.6 mmol) CS_2 and excess HFP were reacted at about 80 °C for 10 days. After evaporation of the volatiles (unreacted CS_2 and HFP), one part of the pale yellow solid residue was dissolved in MeCN, another in diluted hydrochloric acid which was subsequently extracted with ether. The ^{19}F NMR spectra of the solutions showed two signals each, in MeCN an intense signal at − 73 ppm (d, $J = 8.5$ Hz) and a small signal at − 172 ppm (m, $J = 8.6$ Hz), and in ether solution an intense signal at − 73 ppm and a small signal at

− 180 ppm, which can be attributed to the anion of heptafluorodithioisobutyric acid (**2**) and the free acid respectively.

3.4. Reaction with bis(2,2,2-trifluoroethyl)amine (7)

Synthesis of **8**. 95 mg (1 mmol) TMAF and excessive CS_2 and **7** were warmed from − 196 °C to room temperature in the course of about 3 h under repeated shaking, and then for another 1 h kept at about 60 °C. From the reaction mixture the volatiles were distilled off (CS_2 and **7** only), and the residual solid was dissolved in CD_3CN, D_6-DMSO, or in MeCN from which crystals could be obtained too. The following NMR spectra were recorded. ^{19}F NMR in MeCN: -67 ppm (t, $^3J_{FH} = 9.8$ Hz). ^1H NMR in CD_3CN: 5.5 ppm (quart, $^3J_{FH} = 9.3$ Hz), 3.3 ppm (s, Me_4N^+). ^{13}C NMR in D_6-DMSO: 222 ppm (s, CSS^-), 125 ppm (quart, $^1J_{CF} = 283.1$ Hz, CF_3), 54 ppm (t, $^1J_{CN} = 3.6$ Hz, $[CH_3]_4N^+$), 51 ppm (quart, $^2J_{CF} = 32.5$ Hz, CH_2). FAB-MS from DMSO/glycerol: 256 (100%, $[CF_3CH_2]_2NCSS^-$), 586 (13%, $[(CH_3)_4N]^+ \cdot 2\text{-}[(CF_3CH_2)_2NCSS]^-$). All these data are consistent with a tetramethylammonium salt of *N,N*-bis(2,2,2-trifluoroethyl)dithiocarbamic acid (**8**) as formulated. Crystals of **8** from MeCN solution were used to take IR and Raman spectra. IR (cm^{-1}): 3009 m, 2955 m, 1486 s, 1426 m, 1414 m, 1399 m, 1368 s, 1316 vs, 1263 vs, 1232 s, 1163 vs, 1148 vs, 1102 vs, 1016 vs, 956 m, 943 s, 828 m, 685 s, 583 m. Raman (cm^{-1}): 3008 m, 2953 s, 1459 m, 1415 m, 1372 s, 1285 m, 1238 m, 942 m, 824 m, 752 s, 673 m, 609 vs, 528 s, 443 vs, 379 vs, 286 m.

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