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On the reaction of perfluoro-aza-propene with oxygen difluoride and fluorination of bis(trifluoromethyl)-hydroxylamine

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Abstract

The reactions of perfluoro-aza-propene CF_3NCF_2 with an excess of oxygen difluoride OF_2 and the fluorination of bis(trifluoromethyl)hydroxylamine $(CF_3)_2NOH$ are discussed. Additionally, we present density functional calculations $(B3LYP/6-31G^*)$ on bis(trifluoromethyl)-hypofluorite $(CF_3)_2NOF$, which clearly show that this molecule is a model substance for the discussion of negative hyperconjugation. \bigcirc 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Only in few cases are addition reactions of OF_2 described in the literature [1–6]. Recently, we have studied the reaction of OF_2 with perfluoroacetone (CF_3)₂CO, which resulted in the formation of perfluoro(isopropyl)-trifluoroacetyl-peroxide (CF_3)₂C(F)OOC(O)CF₃ (1) [7].

$$2(CF_3)CO + OF_2 \xrightarrow[C_{SF}]{-78^{\circ}C/+25^{\circ}C} (CF_3)_2 C(F)OOC(O)CF_3 + CF_4$$
(1)

We have also reported a new synthesis of perfluoro(2,4dimethyl-3-oxa-2,4-diazapentane) $(CF_3)_2NON(CF_3)_2$ and its characterisation by electron distribution, photo electron spectra and density functional calculations (2) [8–10]

$$2CF_{3}NCF_{2} + OF_{2} \xrightarrow[CsF]{-78^{\circ}C-25^{\circ}C} (CF_{3})_{2}NON(CF_{3})_{2}$$
(2)

The reaction is catalysed by small amounts of CsF and can be explained by an ionic mechanism with the intermediate formation of $(CF_3)_2NOF$ (3–6).

$$CF_3NCF_2 + C_sF \rightarrow C_s^+ N(CF_3)_2^{-}$$
(3)

$$OF_2 + Cs^+ N(CF_3)_2 \xrightarrow{-} (CF_3)_2 NOF + CsF$$
(4)

$$(CF_3)_2NOF + Cs^+N(CF_3)_2 \xrightarrow{-} (CF_3)_2NON(CF_3)_2 + CsF$$
(5)

 $(CF_3)_2NOF + CF_3NCF_2 \rightarrow (CF_3)_2NON(CF_3)_2$ (6)

The preparation of $Cs^+N(CF_3)_2$ ⁻ from CF_3NCF_2 and CsF in (3) is already described in the literature [11]. It makes no difference whether monomeric CF_3NCF_2 or the dimeric form $(CF_3)_2NC(F)$ =NCF₃ is used as starting reagent.

In contradiction to CF₃OOF, which is preparable by reacting an excess of OF₂ with carbonyl fluoride COF_2 and fluorination of CF₃OOH [12,13], the isolation of (CF₃)₂NOF has not yet been reported.

In the following report, we discuss the reactions of CF_3NCF_2 with an excess of OF_2 and the fluorination of $(CF_3)_2NOH$. In order to find a high quality explanation for the formation of the observed reaction products we started intensive calculations, ab initio (HF/6-31G*)-calculations as well as density functional calculations on the B3LYP/6–31G*-level.

2. Experimental

 $(CF_3)_2NOH$ is prepared according to the literature method from NH₃ and CF₃NO [14]. OF₂ was provided by Prof. Sartori, Universität Duisburg.

2.1. Reaction of CF_3NCF_2 with OF_2

0.1 mmol CsF were placed in a 30 ml stainless steel reactor and treated with elemental fluorine (250 mbar). After removing the fluorine 1 mmol CF_3NCF_2 and 5 mmol OF_2

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were condensed. During 48 h the reaction mixture is warmed from -78° C to 25°C in 10°C steps. At -160° C OF₂ and CF₄ were condensed into a cooled glass ampoule (-196° C). The remaining reaction products are trapped by fractional condensation. They were characterised by ¹⁹F-NMR, ¹³C-NMR and vibrational spectra.

Yields (wt.%): (CF₃)₂NON(CF₃)₂: 77; CF₃NO: 12; CF₄: 11.

$$3CF_3NCF_2 \iff 3(CF_3)_2NCs^+ \iff OF_2/-CsF$$

2.2. Reaction of $(CF_3)_2NOH$ with F_2

2.2.1. (*CF*₃)₂*NOH*: *F*₂ 1:1

0.1 mmol CsF were placed in a 30 ml stainless steel reactor and treated with elemental fluorine (250 mbar). After removing the fluorine 1 mmol (CF₃)₂NOH, 2 ml CCl₃F and 1 mmol F₂ were condensed. During 24 h the reaction mixture is warmed slowly from -78° C to 25° C. After separating the reaction products they were characterised as described above.

2.2.2. (CF₃)₂NOH: F₂ 1:5

0.1 mmol CsF were placed in a 30 ml stainless steel reactor and treated with elemental fluorine (250 mbar). After removing the fluorine 1 mmol (CF₃)₂NOH, 2 ml CCl₃F and 5 mmol F₂ were condensed. After 24 h at -78° C the excess of fluorine was removed by pumping at -196° C. After separating the reaction products they were characterised as described above.

Raman Spectra (Jobin-Yvon T 64000, Ar⁺-Laser from Spectra Physics, $\lambda = 514.5$ nm).

IR-spectra (Bruker IFS 113v).

NMR-spectra (Bruker DPX 300) at -60° C in CFCl₃ with CFCl₃ as external standard.

2.2.3. Ab initio calculations

The structure of $(CF_3)_2$ NOF was calculated ab initio with the Hartree–Fock-Method (HF) [15] and density functional with the Becke3LYP-Method [16,17] by using the GAUS-SIAN-94-Package [18]. All calculations were run with 6– 31G* basis sets. B3LYP presents a Density Functional Theory (DFT) method using hybrid functionals. For B3LYP the Becke-3-parameter gradient corrected exchange functional is combined with the gradient-corrected correlation LYP functional by Lee, Yang and Parr. The DFT method is used because it achieves significantly greater accuracy than Hartree–Fock theory by including some of the effects of electron correlation.

3. Results and Discussion

The reaction of CF_3NCF_2 with an excess of OF_2 in the temperature range of -78 to $+25^{\circ}C$ results in the formation of $(CF_3)_2NON(CF_3)_2$, CF_3NO and CF_4 (7). CF_3NO and CF_4 can be regarded as direct decomposition products of the intermediate $(CF_3)_2NOF$. CF_3NO and CF_4 cannot be detected if CF_3NCF_2 and OF_2 are used in a ratio of 2 : 1 [8,9].

$$2(CF_3)(CF_3)_2 \rightarrow 2(CF_3)_2 \rightarrow 2(CF_3)_2$$

The fluorination of $(CF_3)_2$ NOH and F_2 in a ratio of 1 : 1 occurs above 25°C. Hydrogen fluoride is detected by IR spectra in gaseous phase. However no hints for isolated $(CF_3)_2$ NOF are obtained. $(CF_3)_2$ NF, CF_3 NF₂, F_2 CO, CF_3 OF, CF_3 NO and CF_4 are identified as reaction products by ¹⁹F-NMR, ¹³C-NMR and vibrational spectra.

At -78° C a fivefold excess of fluorine is needed to abstract HF. The products are identical with those for the 1 : 1 reaction.

The fluorination experiments lead to the same basic interpretation as the reaction of CF_3NCF_2 with OF_2 . (CF_3)₂NOF is formed intermediately, but its stability does not allow isolation and it decomposes into CF_3NO and CF_4 .

3.1. Calculations

In order to prove this thesis we started intensive calculations on $(CF_3)_2NOF$. In Table 1 the geometry parameters of $(CF_3)_2NOF$ (HF/6-311G* und B3LYP/6-311G*) are presented. The two methods lead to extremely different values, especially the oxygen–fluorine bond length deviates by nearly 20 pm. ($r_{OF HF 6-311G}$ * 137.9 pm, $r_{OF B3LYP 6-311G}$ * 157.7 pm). The density functional method leads to an O–F-distance (157.7 pm), which is not explainable by a classic O–F single bond. In dioxygen difluoride FOOF, a model molecule for negative hyperconjugation, a similar

Table 1 Calculated bond lengths (pm) and angles (°) for $(CF_3)_2NOF$

	HF 6-311G*	B3LYP 6-311G*
rOF	137.9	157.7
rNO	132.4	128.3
rNC	143.6/144.2	147.8/147.0
rCF	129.6-130.8	131.7-133.4
FON	108.8	108.6
ONC	114.2	117.1
CNC	120.7	120.2

	Experimental	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*	MP4SDQ/6-31G*		
rOF	157.5	136.7	149.6	149.3	147.0		
rOO	121.7	131.0	126.5	129.2	132.0		
FOO	109.5	105.8	108.3	106.9	106.2		
FOOF	87.5	84.1	86.7	85.7	85.7		

Table 2 Comparison of experimental [19] and calculated bond lengths (pm) and angles (°) for O_2F_2

Table 3 Calculated bond lengths (pm) and angles (°) for (CF₃)₂NOF (B3LYP/6-311G*) and comparative compounds

	(CF ₃) ₂ NOF	CF ₃ OF [24]	(CF ₃) ₂ NONO [22]	N ₂ O ₅ [23]	(CF ₃) ₂ NOCH ₃ [21]
rOF	157.6	142.1			
rNO	128.3		157.2	149.2	
			141.0		142.4
			115.6	118.3	
rNC	147.3		142.6		142.9
NOF	108.6		107.6		109.4
ONC	117.1		112.1		108.1
CNC	120.2		121.5		118.0

O–F-distance of 158.2 pm was detected by electron distribution [19].

In Table 2 the structural parameters for O_2F_2 , obtained from the B3LYP 6-31G*-calculations, are compared with those previously determined by Oberhammer and Mack from HF/6-31G*, MP2/6-31G* and MP4SDQ/6-31G* calculations [20]. The simple example of O_2F_2 makes clear that the results of the Hartree–Fock-calculations do not correspond with the experimentally determined bond lengths of a hyperconjugated system. The results of the B3LYP-calculations are comparable with the MP2-or MP4SDQ-results, which harmonise with the experimental values [20]. Obviously correlation effects have to be considered in calculations on a hyperconjugated molecule.



Fig. 1. Calculated structure of (CF₃)₂NOF (B3LYP 6-311G*). (a) View on the C-N-C-plane; (b) view along the C-N-bond.

The B3LYP-calculations also fit the experimental values for known $(CF_3)_2NOX$ -compounds e.g. $(CF_3)_2NON(CF_3)_2$ [8,10]. It has to be concluded that this method leads to authentic bond lengths and angles for the target molecule $(CF_3)_2NOF$.

In Table 3 the B3LYP-structural parameters for $(CF_3)_2$ -NOF are compared with those of CF_3OF , $(CF_3)_2NONO$, N_2O_5 and $(CF_3)_2NOCH_3$. The calculated structure of $(CF_3)_2NOF$ is presented in Fig. 1.

The C–N–O-and C–N–C-angles of 117.1 and 120.7° indicate a nearly planar arrangement in $(CF_3)_2NOF$. For $(CF_3)_2NOCH_3$ a C–N–O-angle of 108.1° was determined by electron distribution [21]. The comparison with $(CF_3)_2NONO$ [22] and N_2O_5 [23] shows, that in $(CF_3)_2NOF$ a short N–O-bond of 128.3 pm is present. These facts suggest significant contribution of a 'double bond no bond' component shown by the mesomeric forms in (8) and give an explanation for the observed formation of $CF_3N=O$ and CF_4 in the discussed experiments.

$$(CF_3)_2 N - O - F \leftrightarrow (CF_3)_2 NO^+ F^-$$
(8)

For an appropriate description of the O–F bonding, the electronic interactions in $(CF_3)_2N$ –O–F have to be investigated by a NBO-analysis [25–27].

The concept of the 'Generalised Anomeric Effect' gives a good explanation for the long O–F-distance [28]. The electronic interactions in $(CF_3)_2N$ –O–F are very similar to those in O_2F_2 , where π -contributions to the O–O-bond are responsible for the short O–O-distance of 122 pm and the partial occupation of the $\sigma^*_{(O-F)}$ -orbitals lead to O–F-distances of 158 pm [28,29]. In $(CF_3)_2N$ –O–F the electron pair of the nitrogen atom p-LP(N) interacts with the non-bonding $\sigma^*(O-F)$ -orbitals. By this interaction electron density is transmitted from the p-LP(N) in the $\sigma^*(O-F)$ -orbitals,



Fig. 2. Hyperconjugation in $(CF_3)_2NOF$, orbital contour diagram (+) of overlapping O–F antibond ($\sigma^*_{(O-F)}$) and nitrogen lone pair (p-LP_(N)). The diagram shows an intersection of the F–O–N-plane.

which leads to an O–F-bond weakening and a very long O–F-distance of 157.7 pm. The corresponding NBOs are shown in Fig. 2. A transmittance of electron density from a bonding orbital or a lone pair into a non-bonding orbital is called 'negative hyperconjugation'.

To summarise it has to be pointed out that from the density functional calculations we obtained a good explanation for experimental results. It was shown that $(CF_3)_2NOF$ is model substance for negative hyperconjugation. A possible method for the isolation of this molecule can be seen in the low temperature radical combination of $(CF_3)_2NO^{-7}$ and F^{-7} radicals. O_2F_2 is synthesised on a similar way [30–32].

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