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**PERFLUORINATED DIALKYL PEROXIDES**  
**THEIR PROPERTIES AND SYNTHESSES FROM**  
**PERFLUOROALKYL HYPOHALITES**

Inaugural-Dissertation

to obtain the academic degree  
Doctor rerum naturalium

submitted to the Department of  
Biology, Chemistry, Pharmacy of  
Freie Universität Berlin

Jan Hendrick Nissen  
2020

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für meine Familie

The work for the present dissertation has been conducted between November 2015 and February 2020 under the supervision of Prof. Dr. Sebastian Hasenstab-Riedel at the Institute of Chemistry and Biochemistry at the Department Biology, Chemistry and Pharmacy of Freie Universität Berlin. I certify that this thesis is entirely my own independent work. No other than the declared sources have been used, which are acknowledged as references.

1<sup>st</sup> referee: Prof. Dr. Sebastian Hasenstab-Riedel

2<sup>nd</sup> referee: Prof. Dr. Christian Müller

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Many thanks to my family for your emotional support during my journey, which did not start here at the FU Berlin. You have accompanied me through beautiful and not that beautiful times, you always had an ear for my suffering and you gave me comfort and support, when necessary.

I thank you Luise for your affection, your understanding, your support, your love of the recent years.

## List of Abbreviations

<	angle
aq	aqueous
b.p.	boiling point
BDE	bond dissociation energy
CPBA	chloroperoxybenzoic acid
CCSD(T)	Coupled cluster with single, double and perturbative triple excitations
c-	cyclo
d	days
D	Debye
decomp.	decomposition
BPO	dibenzoyl peroxide
$\Theta$	dihedral angle
DMDO	dimethyldioxirane
e	electron
EA	electron affinity
EPR	electron paramagnetic resonance
eV	electron volt
EN	electronegativity
eq.	equivalent
ES	excited state
e.g.	for example (latin: "exempli gratia")
extrap.	extrapolated
GED	gas-phase electron diffraction
g	gram
GS	ground state
Hal	halogen
hv	high voltage
HOMO	highest occupied molecular orbital
h.p.	high-pressure
h	hours
IR	infrared spectroscopy
IP	ionization potential



<i>i-</i>	iso
LMCT	ligand-to-metal charge transfer
lp	lone pair
LUMO	lowest unoccupied molecular orbital
m	medium
m.p.	melting point
<i>m-</i>	meta
MW	microwave spectroscopy
min	minutes
nm	nanometer
NBO	natural bonding orbital
ND	neutron diffraction
NMR	nuclear magnetic resonance
NPA	natural population analysis
Ph	phenyl
pm	picometer
PFA	poly perfluoroalkoxy-vinyl tetrafluoroethene copolymerisate
<i>q</i>	quaternary
ref.	reference
r.t.	room temperature
MP2	second-order Møller-Plesset perturbation theory
s	seconds
SET	single electron transfer
s	strong
<i>t-, tert-</i>	tertiary
TD-DFT	time-dependend density functional theory
t	ton
UV	ultraviolett
v	very
w	weak
XRD	X-ray diffraction

## Abstract

The present dissertation comprises the preparation of various perfluoroalkyl hypofluorites and hypochlorites and their conversion into the corresponding perfluoro dialkyl peroxides.

A safe and practicable access to highly reactive perfluorinated hypohalites, as suitable precursors for perfluorinated peroxides, is crucial. Hence, a modified synthesis route to the family of hypofluorites including  $F_3COF$ ,  $C_2F_5OF$ ,  $(F_3C)_2FCOF$ ,  $(F_3C)_3COF$  and  $(C_2F_5)(F_3C)_2COF$  is presented. The corresponding hypochlorites  $F_3COCl$ ,  $C_2F_5OCl$ ,  $(F_3C)_2FCOCl$ ,  $(F_3C)_3COCl$  and  $(C_2F_5)(F_3C)_2COCl$  were synthesized and all perfluorinated hypohalites were entirely characterized by NMR and vibrational spectroscopy with the support of quantum-chemical calculations.

A generally applicable transformation of perfluoroalkyl hypofluorites by the treatment with fluorinated silver wool into otherwise difficult to access tertiary perfluoro dialkyl peroxides, e.g. bis(nonafluoro-*tert*-butyl) peroxide,  $[(F_3C)_3CO]_2$ , and bis(undecafluoro-*tert*-pentyl) peroxide,  $[(C_2F_5)(F_3C)_2CO]_2$ , was developed. It was shown, that these peroxides were also obtained by the low-temperature photolysis of the corresponding hypochlorites.

The peroxide compounds were characterized by NMR, gas-phase IR, low-temperature Raman, and UV/Vis spectroscopy. Their chemical properties were investigated, as the perfluorinated dialkyl peroxides are resistant towards acids, dilute elemental halogens and are also insensitive to impact and friction. The solid state structures of  $[(F_3C)_3CO]_2$  and  $[(C_2F_5)(F_3C)_2CO]_2$  were obtained by in situ crystallization. The unusual features for this class of compounds, as dihedral angles along the COOC backbone of  $180^\circ$  and elongated O–O bonds of the peroxide unit, were a result from the bulkiness of the perfluorinated alkyl groups.

## Kurzzusammenfassung

Diese Dissertation umfasst die Darstellung verschiedener perfluorierter Alkylhypofluorite und -hypochlorite und deren Umsetzung zu den entsprechenden Perfluordialkylperoxiden.

Ein sicherer und praktikabler Zugang zu hochreaktiven perfluorierten Hypohalogeniten, welche sich als geeignete Vorläufer für die Synthese von perfluorierten Peroxiden auszeichnen, ist von entscheidender Bedeutung. Daher wurde ein modifizierter Syntheseweg zur Darstellung der Familie der Hypofluorite  $F_3COF$ ,  $C_2F_5OF$ ,  $(F_3C)_2FCOF$ ,  $(F_3C)_3COF$  und  $(C_2F_5)(F_3C)_2COF$  entwickelt. Auch die entsprechenden Hypochlorite  $F_3COCl$ ,  $C_2F_5OCl$ ,  $(F_3C)_2FCOCl$ ,  $(F_3C)_3COCl$  und  $(C_2F_5)(F_3C)_2COCl$  wurden synthetisiert. Die Hypohalogenite wurden durch NMR- sowie schwingungsspektroskopisch unter Zuhilfenahme von quantenchemischen Berechnungen vollständig charakterisiert.

Eine allgemein anwendbare Überführung von Perfluoralkylhypofluoriten durch deren Behandlung mit fluorierter Silberwolle in die ansonsten schwer zugänglichen tertiären Perfluordialkylperoxide Bis(nonafluor-*tert*-butyl)peroxid,  $[(F_3C)_3CO]_2$ , und Bis(undecafluor-*tert*-pentyl)peroxid,  $[(C_2F_5)(F_3C)_2CO]_2$ , wurde entwickelt. Es wurde gezeigt, dass die Peroxide ebenfalls durch Tieftemperaturphotolyse des entsprechenden Hypochlorits zugänglich sind.

Die Peroxide wurden hingehend ihrer NMR-, gasphasen-IR-, tieftemperatur-Raman-, sowie UV/Vis-spektroskopischen Eigenschaften charakterisiert. Die Untersuchung der chemischen Eigenschaften zeigte Beständigkeit gegenüber Säuren. Sie lösen elementare Halogene und sind außerdem unempfindlich gegen äußere Schlag- und Reibungseinwirkung. Durch in-situ Kristallisation wurden die Molekülstrukturen im Festkörper erhalten. Die für diese Verbindungsklasse unübliche Eigenschaften, wie Diederwinkel entlang des COOC Rückgrats von  $180^\circ$ , sowie die verlängerten O–O-Bindungslängen entlang der Peroxideinheit, werden durch den sterischen Anspruch der perfluorierten Alkylgruppen hervorgerufen.

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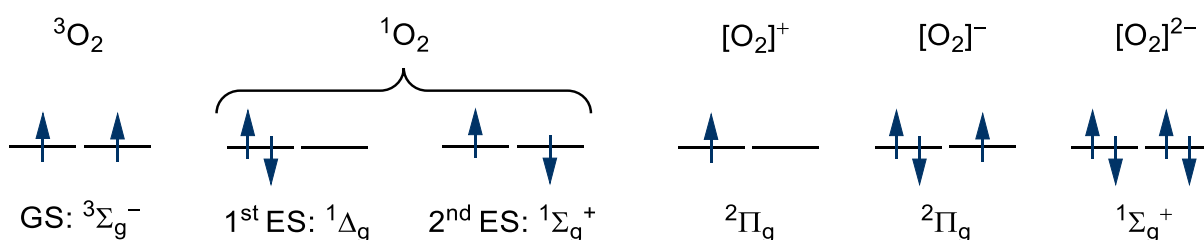
# 1. Introduction

Organic peroxides are compounds of structure ROOR, containing the anion  $[\text{O}_2]^{2-}$ , in which the substituent R may represent any organyl group.<sup>[1]</sup> The oxygen atoms with the oxidation state  $-I$  are connected via a single bond to each other.<sup>[2]</sup> They are formed e.g. in the atmosphere by the reaction of hydrogen or alkyl radicals with dioxygen.<sup>[3]</sup> Hence, dioxygen is the major source of the oxygen atoms in peroxides.

## 1.1. Oxygen and its Modifications

Oxygen is the most abundant element in the earth's crust<sup>[2]</sup> with a mass fraction of 47.4%.<sup>[4]</sup> Together with hydrogen, carbon, nitrogen and phosphorus, oxygen is a primary building block of living cells and therefore said to be by far the most important element. Besides nitrogen, dioxygen is the second most molecule in the atmosphere.<sup>[5]</sup> The main source of atmospheric oxygen is the oxidation of water during photosynthesis.<sup>[3]</sup>

The ground state of  $\text{O}_2$  is the paramagnetic triplet state with two unpaired electrons in the two degenerated antibonding  $2\pi^*$  orbitals ( $^3\text{O}_2$ ,  $S = 2$ ), see Scheme 1.1.<sup>[4]</sup> The distance between the oxygen atoms is 120.8 pm with a bond dissociation energy (BDE) of  $491 \text{ kJ mol}^{-1}$  (Table 1.1).<sup>[2]</sup>  $^3\text{O}_2$  can be excited to more reactive diamagnetic singlet oxygen,  $^1\text{O}_2$ , with two antiparallel orientated electrons in the  $2\pi^*$  orbitals, which can either be paired (1<sup>st</sup> ES) or separated (2<sup>nd</sup> ES). The 2<sup>nd</sup> ES, which is  $158 \text{ kJ mol}^{-1}$  higher in energy in comparison with the triplet state, has a very short lifetime of  $<10^{-9} \text{ s}$  and relaxes to form the 1<sup>st</sup> ES. The significant longer lifetime of  $10^{-4} \text{ s}$  ( $\sim 45 \text{ min}$  at reduced pressure<sup>[4]</sup>) avails the use as a powerful oxidant in chemical syntheses. The excited  $^1\text{O}_2$  relaxes to  $^3\text{O}_2$  by emitting red light with wavelengths of 633 and 703 nm, respectively.

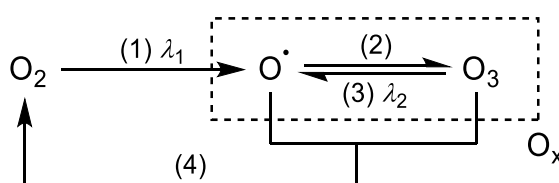


**Scheme 1.1.** Occupation of the two  $2\pi_g^*$  orbitals in modifications of  $\text{O}_2$ .

**Table 1.1.** Electronic configuration and properties of dioxygen and its modifications.

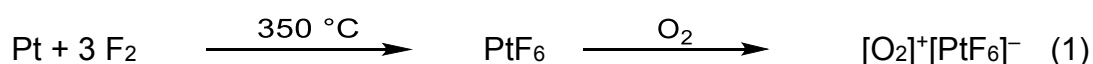
	state	$d(\text{OO})$ [pm]	$(2\pi\text{g}^*)^n$	o.s.	b.o.	BDE [kJ mol <sup>-1</sup> ]
[O <sub>2</sub> ] <sup>+</sup>	<sup>1</sup> Π <sub>g</sub> <sup>+</sup>	111.6 <sup>[4]</sup>	1	+1/2	2.5	643 <sup>[4]</sup>
O <sub>2</sub>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	120.7 <sup>[4]</sup>	2	0	2.0	491 <sup>[4]</sup>
[O <sub>2</sub> ] <sup>-</sup>	<sup>2</sup> Π <sub>g</sub>	135 <sup>[4]</sup>	3	-1/2	1.5	395 <sup>[4]</sup>
[O <sub>2</sub> ] <sup>2-</sup>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	149 <sup>[4]</sup>	4	-1	1.0	126 <sup>[2]</sup>
O <sub>3</sub>	<sup>1</sup> A <sub>1</sub>	127.2 <sup>[6]</sup>	/	0	1.66	300 <sup>[6]</sup>

Ozone, O<sub>3</sub>, is the only further neutral modification of oxygen at adequate pressures. It is formed in the stratosphere at 20 to 30 km altitude by photolysis of O<sub>2</sub> and is essential for terrestrial life, due to its absorption of the UV light emitted by the sun. In the first step of its formation, dioxygen is photolyzed by high-energy photons of wavelengths  $\lambda_1 \leq 240$  nm to form oxygen radicals, O<sup>•</sup>, see Scheme 1.2. This triplet state radicals rapidly react with O<sub>2</sub> to form O<sub>3</sub> by participation of a third body M (most likely N<sub>2</sub> or O<sub>2</sub>), which can remove excess energy and eventually dissipate as heat. Ozone undergoes further photolysis and is in fast equilibrium with O<sup>•</sup>, represented by the O<sub>x</sub> family. Because the O–O bond energy is lower than in O<sub>2</sub>, the required photon energy is lower ( $\lambda_2 \leq 320$  nm). A sink for stratospheric ozone is the reaction with another oxygen radical yielding molecular oxygen, O<sub>2</sub>, as described by Chapman in 1930.<sup>[7]</sup> The O<sub>3</sub> molecule is best represented as a diradical, with a bent structure [ $\angle(\text{OOO}) = 117.5^\circ$ ] and bond lengths of 127 pm,<sup>[6]</sup> slightly longer than that found in O<sub>2</sub>, see Table 1.1. The direct exposure of ozone to solid metal hydroxides, MOH (M = Na, K, Rb, Cs), at reduced temperatures ( $< -10$  °C) yields paramagnetic ozonides, MO<sub>3</sub>.<sup>[2]</sup>

**Scheme 1.2.** The Chapman mechanism.<sup>[3]</sup>

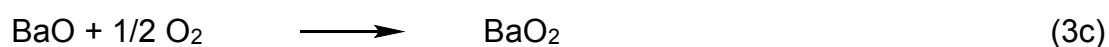
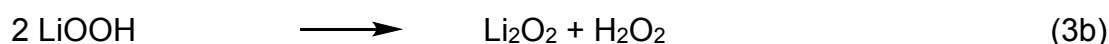
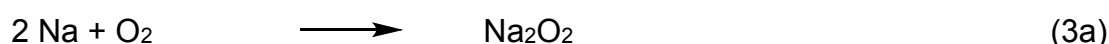
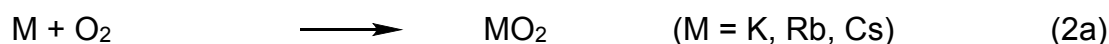
Several ionic modifications of O<sub>2</sub> were investigated in the past. On the one hand, oxidation leads to the dioxygenyl cation, [O<sub>2</sub>]<sup>+</sup>. This was first made possible with the very strong single electron oxidizing reagent platinum hexafluoride, PtF<sub>6</sub>, obtained by the reaction of platinum with elemental fluorine at 350 °C. When PtF<sub>6</sub> is exposed to

oxygen, it readily oxidizes  $O_2$  at room temperature forming the dioxygenyl salt  $[O_2][PtF_6]$ , as shown by Bartlett and Lohmann in 1961 [Equation (1)].<sup>[8]</sup> The dioxygenyl cation,  $[O_2]^+$ , has a higher bond order in comparison with neutral  $O_2$ , which results in an increased BDE ( $643 \text{ kJ mol}^{-1}$ ), and a shorter O–O bond length of 111.6 pm, see Table 1.1. Because of similar first ionization potentials (1<sup>st</sup> IP) of oxygen ( $12.5 \text{ eV} = 1206 \text{ kJ mol}^{-1}$ )<sup>[6]</sup> compared with the noble gas xenon ( $12.13 \text{ eV} = 1170 \text{ kJ mol}^{-1}$ )<sup>[2]</sup>, it also readily reacts with the oxidizing  $PtF_6$  to form a mixture of several cationic xenon compounds.<sup>[9]</sup>



On the other hand, single electron reduction of  $O_2$ , e.g. by an alkali metal M (M = K, Rb, Cs), results in a superoxide anion,  $[O_2]^-$ , see Equation (2a).<sup>[10]</sup> In the case of sodium, the comproportionation of sodium peroxide,  $Na_2O_2$ , with  $O_2$  at elevated temperatures leads to  $NaO_2$  [Equation (2b)].<sup>[10]</sup> Due to the additional electron in the  $2\pi^*$  orbitals (Scheme 1.1), the dissociation energy of  $[O_2]^-$  is reduced to  $395 \text{ kJ mol}^{-1}$  and the O–O distance elongated to 135 pm in comparison with molecular  $O_2$  (Table 1.1).

Oxidation of elemental Na in an oxygen stream leads to the formation of sodium peroxide,  $Na_2O_2$ , [Equation (3a)].<sup>[2]</sup> The single bond of the peroxide dianion,  $[O_2]^{2-}$ , has a distance of 149 pm and a comparably low dissociation energy of  $126 \text{ kJ mol}^{-1}$  (Table 1.1). Other alkali metal or alkaline earth metal peroxides are obtained, e.g. in the case of lithium, from the hydroperoxide,  $LiOOH$  [Equation (3b)], or in the case of barium by oxidation of the oxide,  $BaO$  [Equation (3c)].<sup>[2]</sup>

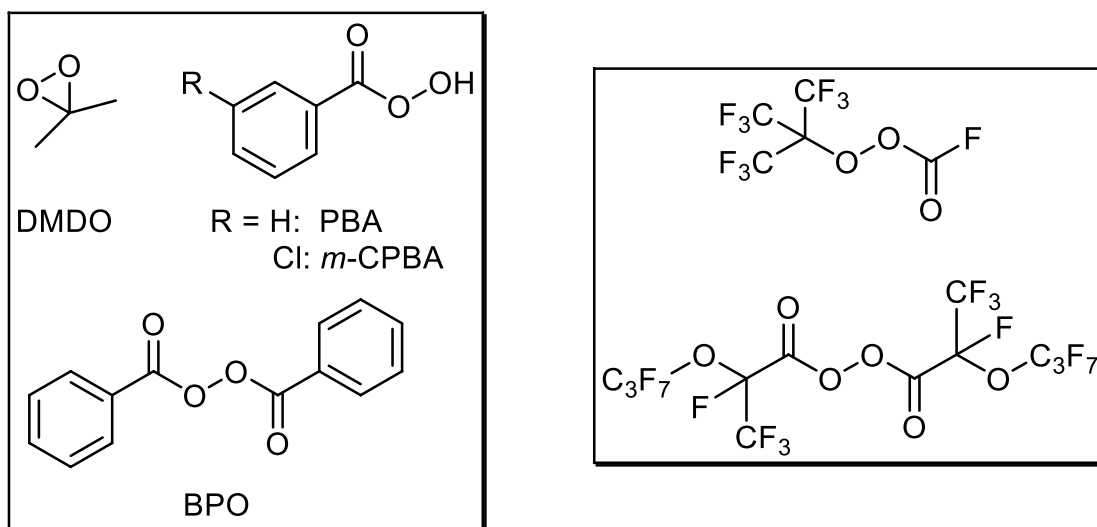


## 1.2. Peroxides

Alkyl peroxide compounds are oxidizing reagents and play an important role in atmospheric chemistry. The prototype dimethyl peroxide,  $(\text{H}_3\text{CO})_2$ , is formed in the stratosphere by oxidation of methane<sup>[11]</sup> and therefore involved in the ozone depletion.<sup>[12]</sup> Peroxide compounds can be divided into five major subgroups:<sup>[5]</sup>

- hydroperoxides (ROOH)
- percarboxylic acids  $[\text{RC}(\text{O})\text{OOH}]$
- peroxy esters  $[\text{RC}(\text{O})\text{OOR}]$
- diacyl peroxides  $[\text{RC}(\text{O})\text{OOC}(\text{O})\text{CR}]$
- dialkyl peroxides (ROOR)

Dioxymethane<sup>[13]</sup> or its methylated variation dimethyldioxirane (DMDO, Figure 1.1),<sup>[14]</sup> are ephemeral small organic peroxides, which oxidize olefins to epoxides with high selectivity.<sup>[15]</sup> Also peroxybenzoic acid (PBA) or its chlorinated isomer *m*-chloroperoxybenzoic acid (*m*-CPBA) are commonly used for oxidation reactions.<sup>[16]</sup> As a representative of a diacyl peroxide, dibenzoyl peroxide (BPO) is well described and widely used, e.g. as a radical starter in polymerization reactions.<sup>[5,17,18]</sup> Furthermore, the related compound class of perfluorinated fluoroformyl peroxides,  $\text{R}^{\text{F}}\text{OOC}(\text{O})\text{F}$  [ $\text{R}^{\text{F}} = \text{C}(\text{CF}_3)_3$ ],<sup>[19]</sup> as well as perfluorodiacyl peroxides,  $\text{R}^{\text{F}}\text{C}(\text{O})\text{OOC}(\text{O})\text{R}^{\text{F}}$  [ $\text{R}^{\text{F}} = \text{CF}(\text{CF}_3)(\text{OC}_3\text{F}_7)$ ], represent important reactants in the industrial synthesis of fluoropolyether chains.<sup>[20]</sup>

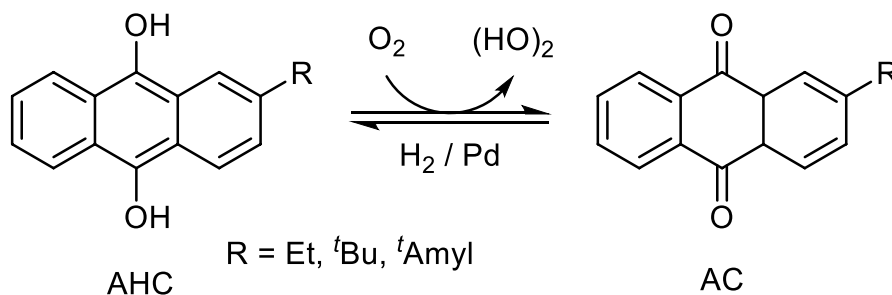


**Figure 1.1.** Structural formulas of some industrially relevant (fluorinated) peroxides.



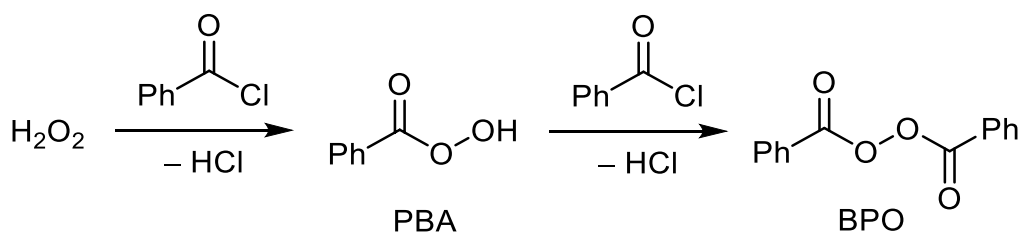
## 1.2.1. Syntheses

The simplest peroxide is hydrogen peroxide,  $(\text{HO})_2$ . This basic chemical is produced in a multiton scale of about 2 700 000 t each year (1998)<sup>[21]</sup>, mainly by the catalytic anthraquinone oxidation process (Scheme 1.3).<sup>[22]</sup> The reversible oxidation of an alkyl anthrahydroquinone, AHC, with atmospheric  $\text{O}_2$  leads to the corresponding alkyl anthraquinone, AC, under the release of  $(\text{HO})_2$ .



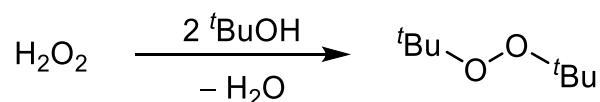
**Scheme 1.3.** Formation of  $(\text{HO})_2$  by oxidation of an alkyl anthrahydroquinone, AHC.

Since the first discovery of the organic peroxide PBA by Brodie in 1858,<sup>[23]</sup> numerous of other peroxides were prepared and characterized. Hydrogen peroxide is the most common precursor for other hydrogen containing peroxides. For example, the reaction of  $(\text{HO})_2$  with benzoyl chloride,  $\text{PhC}(\text{O})\text{Cl}$ , forms PBA<sup>[24,25]</sup> or BPO<sup>[24]</sup>, depending on the stoichiometry (Scheme 1.4).



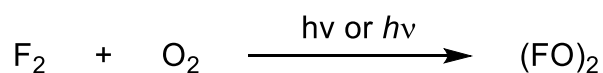
**Scheme 1.4.** Formation of peroxybenzoic acid (PBA) and dibenzoyl peroxide (BPO) by the reaction of  $(\text{HO})_2$  with benzoyl chloride,  $\text{PhC}(\text{O})\text{Cl}$ .

Tertiary alcohols,  ${}^t\text{ROH}$ , are converted into their corresponding dialkyl peroxide,  $({}^t\text{RO})_2$ , by the reaction with  $(\text{HO})_2$  in an acidic milieu, as *tert*-butyl alcohol,  $\text{HOC}(\text{CH}_3)_3$ , provides di-*tert*-butyl peroxide,  $[(\text{H}_3\text{C})_3\text{CO}]_2$  (Scheme 1.5).<sup>[26]</sup>



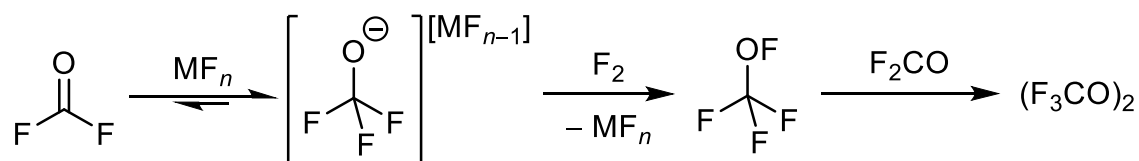
**Scheme 1.5.** Reaction of  $(\text{HO})_2$  with *tert*-butyl alcohol,  $\text{HOC}(\text{CH}_3)_3$ , to yield di-*tert*-butyl peroxide,  $[(\text{H}_3\text{C})_3\text{CO}]_2$ .

The fluorinated counterpart of hydrogen peroxide, difluorine peroxide or dioxygen difluoride,  $(\text{FO})_2$ , is obtained either by high voltage electrical discharge ( $h\nu$ )<sup>[27]</sup> or by UV photolysis ( $h\nu$ )<sup>[28]</sup> at liquid nitrogen temperature of a stoichiometric mixture consisting of elemental oxygen and fluorine (Scheme 1.6).



**Scheme 1.6.** Formation of dioxygen difluoride,  $(\text{FO})_2$ , from fluorine and oxygen.

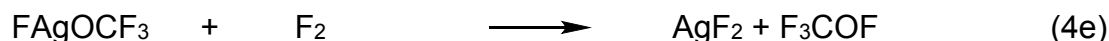
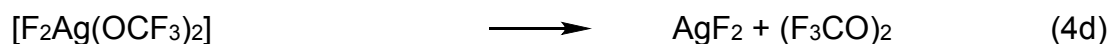
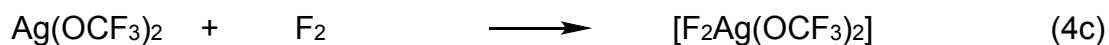
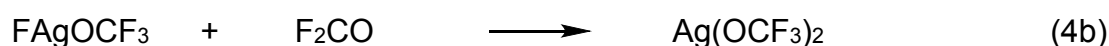
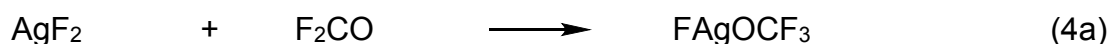
While the syntheses as well as the reactivity of organic, hydrogen containing peroxide compounds are well described, the knowledge about their perfluorinated counterparts,  $(\text{R}^{\text{F}}\text{O})_2$ , is rather scarce. It took almost another century from the discovery of PBA in 1858 for the intended synthesis of bis(trifluoromethyl) peroxide,  $(\text{F}_3\text{CO})_2$ . First observed by Swarts in 1933 by electrolysis of aqueous trifluoroacetic acid in small amounts,<sup>[29]</sup> it were Cady and Porter in 1957, who reacted trifluoromethyl hypofluorite,  $\text{F}_3\text{COF}$ , with carbonyl fluoride,  $\text{F}_2\text{CO}$ , at 250 to 300 °C yielding  $(\text{F}_3\text{CO})_2$ .<sup>[30]</sup> Later, in 1973, Cady and Kennedy used various metal fluorides,  $\text{MF}_n$ , as catalysts ( $\text{MF}_n = \text{BaF}_2, \text{AlF}_3, \text{CuF}_2, \text{NdF}_2, \text{AgF}_2, \text{PrF}_3$ , and others) for the reaction of fluorine,  $\text{F}_2$ , with  $\text{F}_2\text{CO}$  in the temperature range from -78 to 150 °C to obtain  $\text{F}_3\text{COF}$  and/or  $(\text{F}_3\text{CO})_2$ , see Scheme 1.7.<sup>[31]</sup> This reaction was intensively studied in the sixties of the last century by Cady and his co-workers Wechsberg and Kennedy with more than 40 different fluoride salts. Catalysts salts with high ionic character, as alkali earth and alkaline earth metal fluorides, are active at lower temperatures and yield  $\text{F}_3\text{COF}$  almost



**Scheme 1.7.** Metal fluoride catalyzed synthesis of bis(trifluoromethyl) peroxide,  $(\text{F}_3\text{CO})_2$ , from carbonyl fluoride,  $\text{F}_2\text{CO}$ , and fluorine.

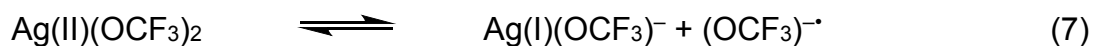
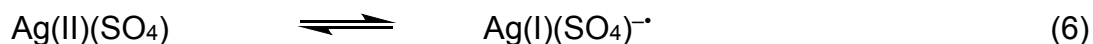
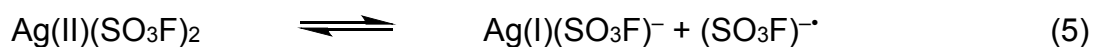
exclusively, while fluorides of transition metals or lanthanides (e.g. AgF, AgF<sub>2</sub>, TbF<sub>3</sub>, BiF<sub>3</sub>, YF<sub>3</sub>, CeF<sub>4</sub> and GdF<sub>4</sub>) yield (F<sub>3</sub>CO)<sub>2</sub> in >90% at temperatures from 25 to 150 °C. From the presented examples, silver difluoride is the most convenient catalyst for this reaction. It was mentioned to provide the highest yield (95%) of the desired peroxide at ambient temperatures (25 °C) within a relatively short reaction time (15 h). Catalysts are poisoned by traces of SiF<sub>4</sub> due to the formation of [SiF<sub>6</sub>]<sup>2-</sup>.

Different mechanisms were proposed for this reaction involving either an ionic or a radical pathway. Wechsberg suggested a stepwise insertion of F<sub>2</sub>CO into the Ag–F bonds forming the silver(II) dialkoxide, Ag(OCF<sub>3</sub>)<sub>2</sub> [Equation (4a,b)].<sup>[32]</sup> Additional fluorination leads to a formal Ag(IV) compound [Equation (4c)], which then releases (F<sub>3</sub>CO)<sub>2</sub> by reductive elimination [Equation (4d)]. Small quantities of F<sub>3</sub>COF could be formed in the side-reaction of fluoro(trifluoromethoxy) argentate(II), FAgOCF<sub>3</sub>, with fluorine [Equation (4e)].

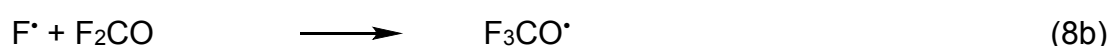
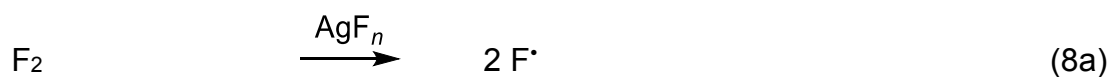


The formulation of an intermediate silver(II) dialkoxide is reasonable due to its high 2<sup>nd</sup> IP (21.46 eV)<sup>[33]</sup>, comparable to that of Xe (21.22 eV) and the halogen bromine (21.80 eV).<sup>[34]</sup> Hence, due to the very strong oxidizing properties of the [Kr]4d<sup>9</sup> coinage metal “*Ag(II) is incompatible with many common inorganic and organic anionic ligands*”.<sup>[34]</sup> For example, silver(II) oxide, AgO, is a mixed-valaced compound Ag(I)[Ag(III)O<sub>2</sub>] and the thermal instability of silver difluorosulfonate, Ag(II)(SO<sub>3</sub>F)<sub>2</sub>,<sup>[35]</sup> and silver sulfate, Ag(II)SO<sub>4</sub> (*T*<sub>decomp.</sub> > 120 °C)<sup>[36]</sup>, can be explained by transfer of spin density from the metal to the ligand, as described by their electromeric equilibria between the ionic structure and ‘free’ radicals in Equations (5) and (6), respectively.<sup>[34]</sup> In the case of silver sulfate, a partial bond (b.o. = 1/2) among the oxygen atoms of the tautomeric radical anion (SO<sub>4</sub>)<sup>-</sup>.<sup>[34]</sup> Considering the catalytic formation of (F<sub>3</sub>CO)<sub>2</sub>, the postulated metastable Ag(II)(OCF<sub>3</sub>)<sub>2</sub> may in fact undergo a similar ligand-to-metal

charge transfer (LMCT) [Equation (7)] and is therefore prone to preform the oxygen-oxygen single bond of the subsequently released bis(trifluoromethyl) peroxide.

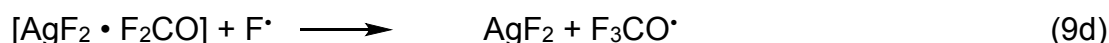
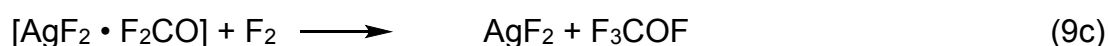
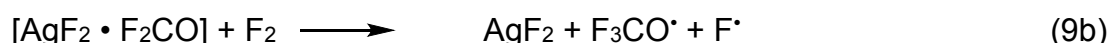
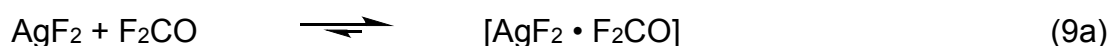


In contrast to an ionic reaction pathway, Cady advocated a homolytic bond cleavage of fluorine, catalyzed by silver fluorides,  $\text{AgF}_n$  ( $n = 1, 2$ ), with subsequent formation of a trifluoromethoxy radical,  $\text{F}_3\text{CO}^\cdot$  [Equations (8a,b)]. Such a radical may either combine with another methoxy radical to yield  $(\text{F}_3\text{CO})_2$ , or react with a fluorine radical forming  $\text{F}_3\text{COF}$  [Equations (8c,d)].<sup>[31]</sup> This radical mechanism is adopted by the prior work of Schumacher and co-workers, photolysing a mixture of sulfur trioxide,  $\text{SO}_3$ , and  $\text{F}_2$  to yield either fluorine fluorosulfate,  $\text{FSO}_2\text{OF}$ , or with excess  $\text{SO}_3$ , bis(fluorosulfonyl) peroxide,  $(\text{FSO}_2\text{O})_2$ , respectively, also called peroxydisulfonyldifluorid.<sup>[37]</sup> When reaction (8b) is fast compared with the competitive reaction (8d), a higher concentration of  $\text{F}_2\text{CO}$  certainly leads to a higher yield of bis(trifluoromethyl) peroxide.

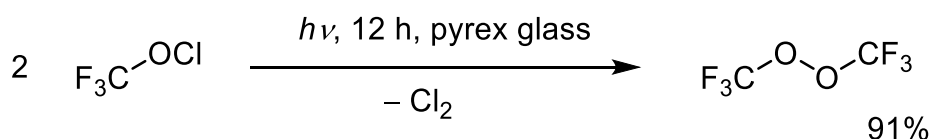


Kinetic studies on the thermal decomposition of the peroxide  $(\text{F}_3\text{CO})_2$  into  $\text{F}_2\text{CO}$  and  $\text{F}_3\text{COF}$  performed by Kennedy and Levy,<sup>[38,39]</sup> revealed that the rate of production of  $(\text{F}_3\text{CO})_2$  from  $\text{F}_2\text{CO}$  with  $\text{F}_2$  in the presence of  $\text{AgF}_n$  is about 10 000 times greater than expected. Hence, reactions (8a) and (8b) do not provide enough  $\text{F}_3\text{CO}^\cdot$  for the amount of obtained peroxide  $(\text{F}_3\text{CO})_2$  with the result that the metal fluoride plays a more central role than catalyzing the homolytic bond cleavage of fluorine. Therefore, Kennedy proposed that the catalyst, e.g.  $\text{AgF}_2$ , adsorbs  $\text{F}_2\text{CO}$  by  $\pi$ -bonding in an equilibrium with distortion of the carbonyl group to form the complex  $[\text{AgF}_2 \cdot \text{F}_2\text{CO}]$  as the active species [Equation (9a)].<sup>[31]</sup> The successive reaction of the complex with  $\text{F}_2$  is competitive and yields either  $\text{F}_3\text{CO}^\cdot$ , together with  $\text{F}^\cdot$  [Equation (9b)], or  $\text{F}_3\text{COF}$  via an one-step addition of  $\text{F}_2$  [Equation (9c)], depending on the catalysts' nature.<sup>[31]</sup> The

released fluorine radicals can react with the  $[\text{AgF}_2 \cdot \text{F}_2\text{CO}]$  complex generating more  $\text{F}_3\text{CO}^\bullet$  radicals [Equation (9d)], which react further to form  $(\text{F}_3\text{CO})_2$  and  $\text{F}_3\text{COF}$ , respectively, as described by reactions (9c,d). It was assumed, that the dissociation of  $\pi(\text{CO})$  is the most important barrier for the reaction of fluorine with gaseous  $\text{F}_2\text{CO}$ .<sup>[31]</sup> In the adsorbed species,  $[\text{AgF}_2 \cdot \text{F}_2\text{CO}]$ , the planar configuration of the ketone may be distorted, which exhibits the  $\pi$ -bond orbitals and the reaction with fluorine is more susceptible to reveal a great amount of trifluoromethoxy radicals quickly.<sup>[31]</sup>



Simultaneously to the reactivity studies of the hypofluorite  $\text{F}_3\text{COF}$  with  $\text{F}_2\text{CO}$  by Cady and co-workers, Schack and Maya developed the reactivity of trifluoromethyl hypochlorite,  $\text{F}_3\text{COCl}$ , in 1969. Photolysis of  $\text{F}_3\text{COCl}$  at room temperature leads to trifluoromethoxy radicals,  $\text{F}_3\text{CO}^\bullet$ ,<sup>[40]</sup> which dimerize to provide the symmetrically substituted bis(trifluoromethyl) peroxide in 91% yield (Scheme 1.8). Hence, both, the trifluoromethyl hypofluorite, and the hypochlorite, are therefore suitable precursors for the synthesis of  $(\text{F}_3\text{CO})_2$ .



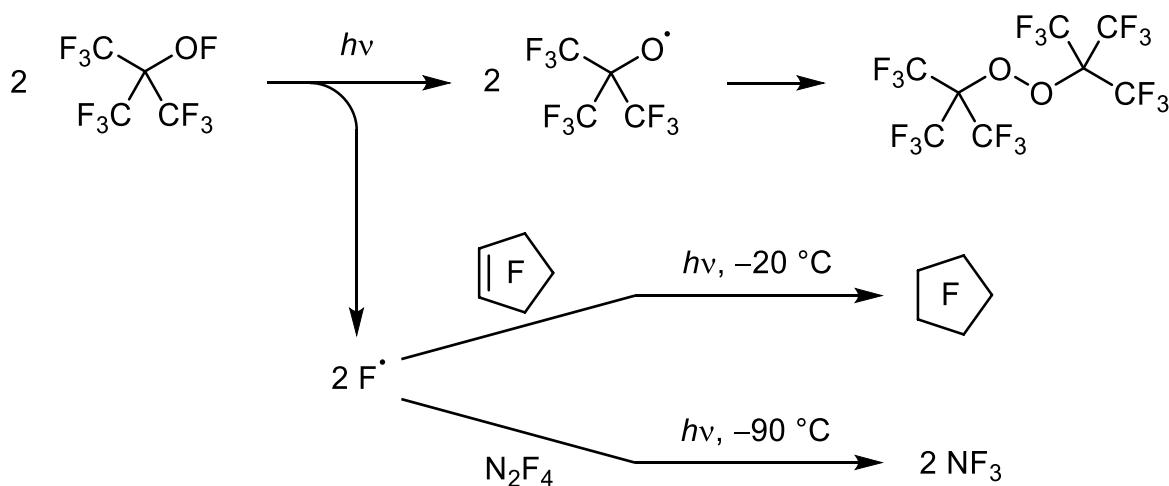
**Scheme 1.8.** Irradiation of trifluoromethyl hypochlorite,  $\text{F}_3\text{COCl}$ , to yield bis(trifluoromethyl) peroxide,  $(\text{F}_3\text{CO})_2$ , and chlorine,  $\text{Cl}_2$ .

The bulkier substituted bis(nonafluoro-*tert*-butyl) peroxide,  $[(\text{F}_3\text{C})_3\text{CO}]_2$ , was first obtained and partially described in 1970 by Gould, Ratcliffe and Anderson.<sup>[41]</sup> The reaction of stoichiometric amounts of chlorine trifluoride,  $\text{ClF}_3$ , and nonafluoro-*tert*-butyl alcohol,  $\text{HOC}(\text{CF}_3)_3$ , in a high-pressure stainless steel vessel leads to  $[(\text{F}_3\text{C})_3\text{CO}]_2$  in 50 to 70% yield (Scheme 1.9).



**Scheme 1.9.** Synthesis of bis(nonafluoro-*tert*-butyl) peroxide,  $[(\text{F}_3\text{C})_3\text{CO}]_2$ , from the reaction of nonafluoro-*tert*-butyl alcohol,  $\text{HOC}(\text{CF}_3)_3$ , with chlorine trifluoride,  $\text{ClF}_3$ .

Later in 1976, Toy and Stringham showed that  $[(\text{F}_3\text{C})_3\text{CO}]_2$  is also obtained by irradiation of nonafluoro-*tert*-butyl hypofluorite,  $(\text{F}_3\text{C})_3\text{COF}$ , in the presence of a fluorine atom acceptor at lower temperatures.<sup>[42]</sup> Photolysis of the hypofluorite at  $-20^\circ\text{C}$  readily provides fluorine radicals,  $\text{F}^\cdot$ , and alkoxy radicals,  $(\text{F}_3\text{C})_3\text{CO}^\cdot$ ,<sup>[43]</sup> which then combine to form the oxygen-oxygen bond of bis(nonafluoro-*tert*-butyl) peroxide (Scheme 1.10). The fluorine atoms e.g. add to the double bond of octafluorocyclopentene, *c*- $\text{C}_5\text{F}_8$ , forming the corresponding cycloalkane, or provide trifluoroamine,  $\text{NF}_3$ , by the reaction with tetrafluorohydrazine,  $\text{N}_2\text{F}_4$ .<sup>[42]</sup>



**Scheme 1.10.** Synthesis of bis(nonafluoro-*tert*-butyl) peroxide,  $[(\text{F}_3\text{C})_3\text{CO}]_2$ , by irradiation of nonafluoro-*tert*-butyl hypofluorite,  $(\text{F}_3\text{C})_3\text{COF}$ , in the presence of a fluorine atom acceptor as octafluorocyclopentene, *c*- $\text{C}_5\text{F}_8$ , or tetrafluorohydrazine,  $\text{N}_2\text{F}_4$ .

In contrast to the reaction of nonafluoro-*tert*-butyl hypofluorite, irradiation of the trifluoromethyl substituted hypohalites  $\text{F}_3\text{COF}$  or  $\text{F}_3\text{COCl}$  in the presence of  $\text{N}_2\text{F}_4$  does not yield the peroxide  $(\text{F}_3\text{CO})_2$ , but instead difluoroaminoxytrifluoromethane,  $\text{F}_3\text{CONF}_2$ , and  $\text{NF}_3$  or chlorine,  $\text{Cl}_2$ , respectively.<sup>[40,44]</sup>

## 1.2.2. Properties and Reactivities

The introduction of fluorine atoms to organic compounds often significantly modifies their physicochemical properties and reactivity. For example, the boiling point of (HO)<sub>2</sub> (b.p. = 153 °C, see Table 1.2) is drastically decreased by 210 K in comparison with its fluorinated counterpart (FO)<sub>2</sub> (b.p.<sub>extrap.</sub> = -57 °C)<sup>[45]</sup>. A further peculiarity is the thermal stability of (HO)<sub>2</sub> at ambient temperatures, while (FO)<sub>2</sub> decomposes above -95 °C.<sup>[45]</sup> For (FO)<sub>2</sub>, the required energy for O–O bond dissociation (293 kJ mol<sup>-1</sup>, Table 1.2) is way higher than that for O–F bond cleavage (78 kJ mol<sup>-1</sup>)<sup>[46]</sup>. This is even lower than of elemental fluorine (BDE = 155 kJ mol<sup>-1</sup>)<sup>[46]</sup>, which makes this peroxide a very potent fluorination reagent. The addition of organic compounds, such as ethanol, benzene or methane, often leads to violent explosions and flame appearance even at temperatures around its melting point (-160 °C, Table 1.2).<sup>[47]</sup>

The discrepancy of the boiling points of the methyl substituted peroxides (H<sub>3</sub>CO)<sub>2</sub> (14 °C)<sup>[48]</sup> and (F<sub>3</sub>CO)<sub>2</sub> (-37 °C)<sup>[49]</sup>, respectively, is explained by decreased intramolecular interactions for the fluorinated molecule. Furthermore, while liquid (H<sub>3</sub>CO)<sub>2</sub> is described to act wholesome, its gas demonstrates violent and spontaneous decomposition behavior, comparable to that of the ignition of a H<sub>2</sub> / Cl<sub>2</sub> mixture.<sup>[48]</sup> In contrast, (F<sub>3</sub>CO)<sub>2</sub> is extraordinary resistant and thermally stable up to 200 °C.<sup>[11]</sup>

The very different attributes of the simple dialkyl peroxides (H<sub>3</sub>CO)<sub>2</sub> and (F<sub>3</sub>CO)<sub>2</sub>, respectively, is not only attributed to their different BDEs for homolytic O–O bond cleavage. The bond energy of the peroxide unit in (F<sub>3</sub>CO)<sub>2</sub> was estimated by low pressure pyrolysis<sup>[50]</sup> to 199 ± 2 kJ mol<sup>-1</sup> and is slightly higher than that of non-fluorinated dialkyl peroxides, (RO)<sub>2</sub> (~160 kJ mol<sup>-1</sup>, see Table 1.2). The average X–X

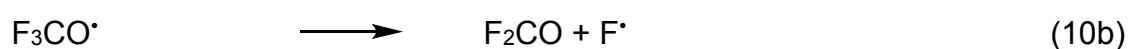
**Table 1.2.** Selected properties of peroxides (RO)<sub>2</sub>.

R	m.p. [°C]	b.p. [°C]	BDE(OO) [kJ mol <sup>-1</sup> ]	ref.
H	-0.43	153	213.8 ± 2.1	[46]
F	-160	-57 <sup>[a]</sup>	293 ± 42	[39]
H <sub>3</sub> C	<-90	13.5	157.3 ± 8.4	[48,51]
F <sub>3</sub> C	<-150	-37	198.7 ± 2.1	[49,50]
(H <sub>3</sub> C) <sub>3</sub> C	-40	111	179.6 ± 4.5	[52,53]
(F <sub>3</sub> C) <sub>3</sub> C	/	99 <sup>[b]</sup>	148.7 ± 4.4 <sup>[c]</sup>	[41,54]

[a] Extrapolated, decomposition at  $T > -95$  °C. [b] The boiling point is accompanied by decomposition. [c] Note text passage.

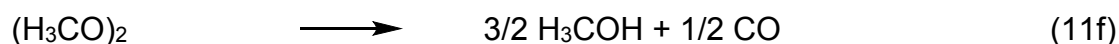
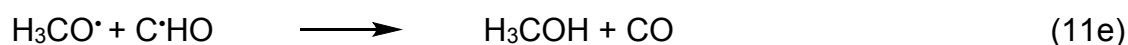
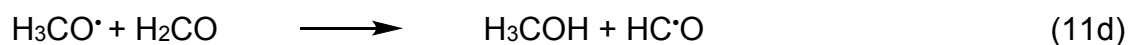
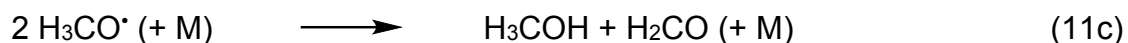
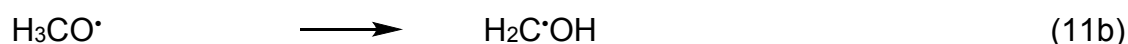
single bond energy of oxygen is low compared with that of the heavier chalcogens sulfur, ( $240 \text{ kJ mol}^{-1}$ ) and selenium, ( $180 \text{ kJ mol}^{-1}$ ) and more comparable to the energy of the heavy homologous tellurium ( $142 \text{ kJ mol}^{-1}$ ).<sup>[11]</sup> Due to the increasing covalent radii and the accompanied increase of the bond length within the group, the effect of the lone pair repulsion becomes much smaller. This results in a relatively low BDE of the O–O single bond in peroxides RO–OR, which is almost independent of the nature of the substituent R.<sup>[5,50,55]</sup> Therefore, the bond cleavage requires a comparatively low thermal energy and can also easily be initiated catalytically, often causing a very exothermic decomposition reaction, which may lead to an explosion or even detonation.<sup>[17]</sup> Even though, as mentioned by Rieche in 1958, the larger the organic groups attached to the peroxide, the more harmless it will be. Additionally, if a peroxide group is gathered by a small and a large organic group, the larger one determines its temperament.<sup>[56]</sup> Hence, di-*tert*-butyl peroxide,  $[(\text{H}_3\text{C})_3\text{CO}]_2$ , is one of the most stable organic dialkyl peroxide and can be handled as a harmless liquid.<sup>[26]</sup> More recently, BDEs for the homolytic O–O bond cleavage were investigated in a broader scope by several computational studies.<sup>[50,55,57]</sup>

The versatile use in chemical synthesis and industrial processes as catalyst and activators of such (fluorinated) dialkyl peroxides,  $(\text{R}^{(\text{F})}\text{O})_2$ , is based on their ability to break the peroxy bond in a clean way<sup>[11]</sup> to form alkoxy radicals,  $\text{R}^{(\text{F})}\text{O}^\cdot$ .<sup>[16,56]</sup> This was confirmed by EPR studies at low temperatures ( $-196 \text{ }^\circ\text{C}$  to  $-170 \text{ }^\circ\text{C}$ ) during the irradiation of  $(\text{F}_3\text{CO})_2$ .<sup>[58]</sup> While kinetic studies<sup>[39,59]</sup> on the thermal decomposition of the peroxides  $(\text{F}_3\text{CO})_2$  and  $(\text{H}_3\text{CO})_2$ , respectively, reveal comparable rates for the initial homolytic cleavage of the O–O bond [Equation (10a):  $\log A = 15.2 \text{ s}^{-1}$  vs. Equation (11a):  $\log A = 15.6 \text{ s}^{-1}$ , both with minor dependence on the temperature],<sup>[11]</sup> the main difference between their decomposition behavior is due to secondary reactions of the initially formed alkoxy radicals,  $\text{R}^{(\text{F})}\text{O}^\cdot$ . On the one hand, the abstraction of a fluorine atom of  $\text{F}_3\text{CO}^\cdot$  [Equation (10b)] is slow<sup>[39]</sup> and the overall decomposition of



$$\Delta H^\circ = 102.5 \pm 2.9 \text{ kJ mol}^{-1}$$





$$\Delta H^\circ = -231 \text{ kJ mol}^{-1}$$

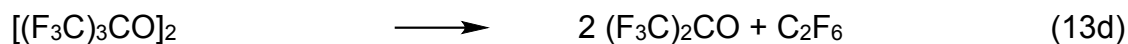
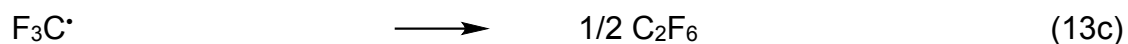
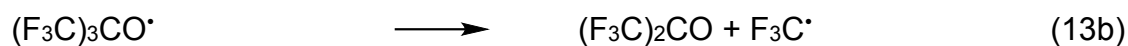
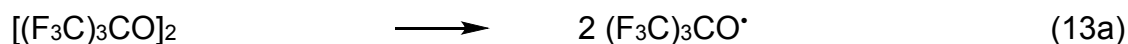
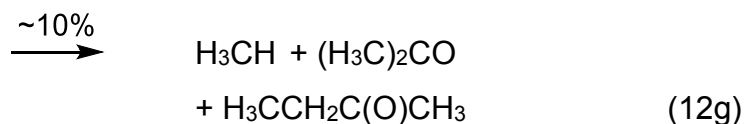
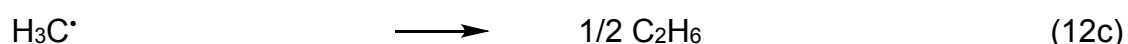
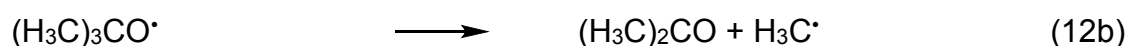
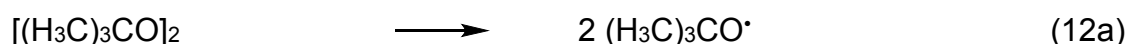
$(\text{F}_3\text{CO})_2$  yielding  $\text{F}_3\text{COF}$  and  $\text{F}_2\text{CO}$  [Equation (10d)] is endothermic by  $\Delta H^\circ = 102.5 \pm 2.9 \text{ kJ mol}^{-1}$ .<sup>[11]</sup> On the other hand, the secondary reactions of dimethyl analogue  $(\text{H}_3\text{CO})_2$  are fast<sup>[60]</sup> and its overall decomposition to methanol,  $\text{H}_3\text{COH}$ , and carbon monoxide,  $\text{CO}$ , is exothermic [ $\Delta H^\circ = -231.0 \text{ kJ mol}^{-1}$ , Equation (11f)].<sup>[11]</sup> The initially formed methoxy radical,  $\text{H}_3\text{CO}^\bullet$ , can either isomerize [Equation (11b)] or react to methanol,  $\text{H}_3\text{COH}$ , and formaldehyde,  $\text{H}_2\text{CO}$ , as described in Equation (11c), which probably involves a third body  $\text{M}$ .<sup>[11]</sup> The release of a hydrogen atom from  $\text{H}_3\text{CO}^\bullet$  in analogy to  $\text{F}_3\text{CO}^\bullet$  [Equation (10b)] is too slow and negligible.<sup>[59]</sup>  $\text{H}_2\text{CO}$  reacts further to produce  $\text{CO}$  [Equations (11d,e)], whose extraordinary high vapour pressure (20 bar at  $-152 \text{ }^\circ\text{C}$ )<sup>[61]</sup> accompanied by the strongly exothermic overall reaction (11f) professes the violent decomposition of gaseous  $(\text{H}_3\text{CO})_2$ .

For the bulkier substituted homologues di-*tert*-butyl peroxide,  $[(\text{H}_3\text{C})_3\text{CO}]_2$ , and its fluorinated analogue bis(nonafluoro-*tert*-butyl) peroxide,  $[(\text{F}_3\text{C})_3\text{CO}]_2$ , the initial step of the thermal decomposition is the homolytic O–O bond cleavage,<sup>[54]</sup> to form *tert*-butoxy radicals  $(\text{H}_3\text{C})_3\text{CO}^\bullet$  [Equation (12a)] and  $(\text{F}_3\text{C})_3\text{CO}^\bullet$  [Equation (13a)], respectively. This is the rate-determining step of the following reaction sequence.<sup>[11]</sup>

For  $(\text{H}_3\text{C})_3\text{CO}^\bullet$ , the radical then undergoes  $\beta$ -C–C bond cleavage to yield acetone,  $(\text{H}_3\text{C})_2\text{CO}$ , and methyl radicals,  $\text{H}_3\text{C}^\bullet$ , which subsequently combine to ethane,  $\text{C}_2\text{H}_6$ , [Equations (12b,c)]. This predominant reaction of  $[(\text{H}_3\text{C})_3\text{CO}]_2$  is summarized in Equation (12f). Concomitant, in side reactions of about 10%, methyl radicals abstract  $\beta$ -hydrogen atoms of  $(\text{H}_3\text{C})_2\text{CO}$  to form methane,  $\text{CH}_4$ , and the radical  $\text{H}_2\text{C}^\bullet\text{C}(\text{O})\text{CH}_3$  [Equation (12d)], which combines with  $\text{H}_3\text{C}^\bullet$  yielding 2-butanone,  $\text{H}_3\text{CCH}_2\text{C}(\text{O})\text{CH}_3$  [Equation (12e)]. This side reaction of  $[(\text{H}_3\text{C})_3\text{CO}]_2$  is compiled in Equation (12g). The high temperature pyrolysis in the range of 360 to 623 K of neat  $[(\text{H}_3\text{C})_3\text{CO}]_2$  was investigated by numerous workers in the middle of the last century, which resulted in

a BDE for the peroxide unit [Equation (12a)] of 155 to 162 kJ mol<sup>-1</sup> with a corresponding log A = 15 to 16 s<sup>-1</sup>.<sup>[62]</sup> The early kinetic studies deviate from photoacoustic calorimetry investigations in 2001.<sup>[52]</sup> The photolysis of [(H<sub>3</sub>C)<sub>3</sub>CO]<sub>2</sub> in solution at r.t., led to an adapted dissociation energy for O–O bond cleavage of 179.6 ± 4.5 kJ mol<sup>-1</sup> (see Table 1.2).<sup>[52]</sup>

In principle, compared with the decomposition of (H<sub>3</sub>C)<sub>3</sub>CO<sup>•</sup>, the fluorinated (F<sub>3</sub>C)<sub>3</sub>CO<sup>•</sup> radical reveals similar reactions yielding hexafluoroacetone, (F<sub>3</sub>C)<sub>2</sub>CO, and the trifluoromethoxy radical, F<sub>3</sub>CO<sup>•</sup> [Equation (13b)],<sup>[54]</sup> which then combine to hexafluoroethane, C<sub>2</sub>F<sub>6</sub>, [Equation (13c)]. In contrast to H<sub>3</sub>C<sup>•</sup> radicals, the abstraction of a fluorine atom by F<sub>3</sub>C<sup>•</sup> radicals from (F<sub>3</sub>C)<sub>2</sub>CO is very slow, so the analogous reactions (12d) and (12e) are not present in the reaction pathway of the fluorinated peroxide [(F<sub>3</sub>C)<sub>3</sub>CO]<sub>2</sub>. Hence, its overall decomposition exclusively yields (F<sub>3</sub>C)<sub>2</sub>CO and C<sub>2</sub>F<sub>6</sub>, as described by Equation (13d).



In contrast to the well studied non-fluorinated [(H<sub>3</sub>C)<sub>3</sub>CO]<sub>2</sub>, the kinetic of the decomposition of its perfluorinated counterpart [(F<sub>3</sub>C)<sub>3</sub>CO]<sub>2</sub> was investigated once in 1977 by pyrolysis in the temperature range from 108 to 149 °C.<sup>[54]</sup> Its decomposition was found to be a homogeneous reaction of first order and the BDE of the peroxide unit was determined to 148.7 ± 4.4 kJ mol<sup>-1</sup> (log A = 16.2 ± 1.2 s<sup>-1</sup>, see Table 1.2). The BDE

was compared with that of  $[(\text{H}_3\text{C})_3\text{CO}]_2$  (BDE =  $179.6 \pm 4.5$  kJ mol<sup>-1</sup>, Table 1.2) and the authors concluded that the lifetime of both *tert*-butoxy radicals  $(\text{H}_3\text{C})_3\text{CO}^\bullet$  and  $(\text{F}_3\text{C})_3\text{CO}^\bullet$  are comparable, and the inductive effect of the fluorine atoms have a negligible effect on the electron density of the peroxide group. Indeed, a population analysis by the natural bonding orbital (NBO) approach at B3LYP/6-31G(d,p) level<sup>[63]</sup> revealed comparable occupations for  $\sigma(\text{OO}')$  of 1.99 e for the non-fluorinated peroxides  $(\text{H}_3\text{CO})_2$  and  $[(\text{H}_3\text{C})_3\text{CO}]_2$ , and a slightly lower occupation of 1.97 e for the fluorinated  $(\text{F}_3\text{CO})_2$ , see Figure 1.2. The occupation of the lone pairs  $n_\pi(\text{O})$  and  $n_\pi(\text{O}')$  is reduced due to the electron withdrawing effects of fluorine by 2% from 1.96 e in  $(\text{H}_3\text{CO})_2$  to 1.92 e in  $(\text{F}_3\text{CO})_2$ .<sup>[63]</sup> Since the latest study<sup>[52]</sup> on the decomposition of  $[(\text{H}_3\text{C})_3\text{CO}]_2$  by photoacoustic calorimetry revealed a BDE of about 20 kJ mol<sup>-1</sup> higher than previous investigations by high temperature pyrolysis, the similarly determined energy for the O–O bond cleavage of  $[(\text{F}_3\text{C})_3\text{CO}]_2$  remains questionable.

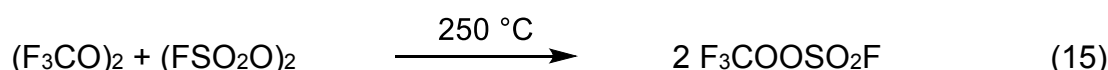
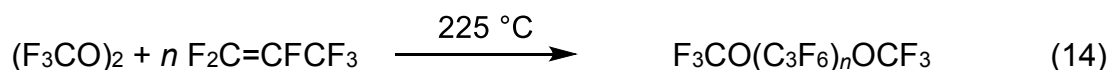
	$\text{H}_3\text{C}-\text{O}-\text{O}-\text{CH}_3$	$(\text{H}_3\text{C})_3\text{C}-\text{O}-\text{O}-\text{C}(\text{CH}_3)_3$	$\text{F}_3\text{C}-\text{O}-\text{O}-\text{CF}_3$
$\sigma(\text{OO}')$ :	1.9864	1.9863	1.9749
$n_\pi(\text{O})$ :	1.9564	1.9588	1.9206

**Figure 1.2.** Population of  $\sigma(\text{OO}')$  and  $n_\pi(\text{O})$  (in e units) for the peroxides  $(\text{H}_3\text{CO})_2$ ,  $[(\text{H}_3\text{C})_3\text{CO}]_2$  and  $(\text{F}_3\text{CO})_2$  by the NBO approach at B3LYP/6-31G(d,p) level.<sup>[63]</sup>

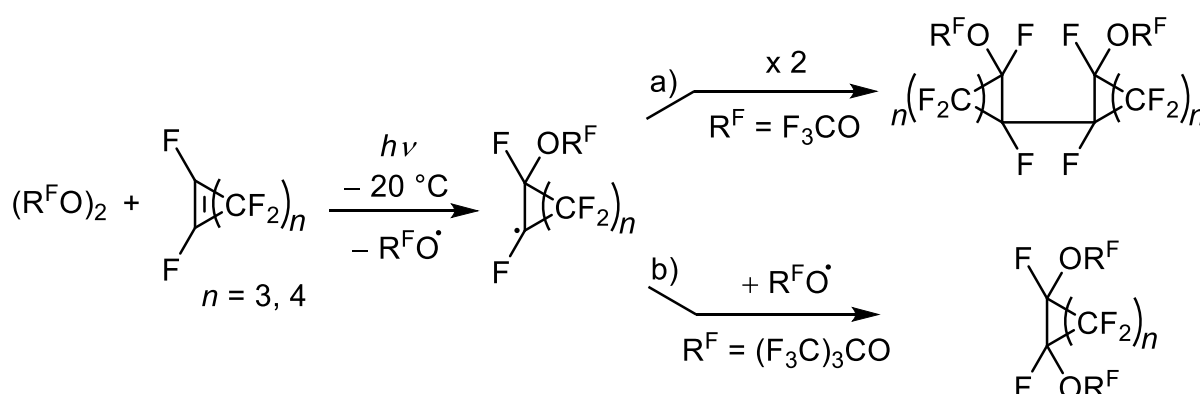
The two symmetrical substituted perfluorinated dialkyl peroxides  $(\text{F}_3\text{CO})_2$  and  $[(\text{F}_3\text{C})_3\text{CO}]_2$  are the only perfluorinated peroxides known so far. For  $(\text{F}_3\text{CO})_2$ , NMR spectra<sup>[64]</sup> and the gas-phase IR and low temperature Raman bands<sup>[65]</sup> are well documented and assigned. For  $[(\text{F}_3\text{C})_3\text{CO}]_2$ , the <sup>19</sup>F NMR and the four strongest absorptions in the mid-IR spectrum (1290, 1110, 1008 and 988 cm<sup>-1</sup>) were reported without any assignment.<sup>[41]</sup>

The reactivity of perfluorinated dialkyl peroxides,  $(\text{R}^{\text{F}}\text{O})_2$ , is sparsely investigated and limited to thermal and photochemical reactions with olefins, such as hexafluoropropene,  $\text{F}_2\text{C}=\text{CFCF}_3$ ,<sup>[49]</sup> perfluorocycloolefins, e.g. *c*- $\text{C}_5\text{F}_8$  and *c*- $\text{C}_6\text{F}_{10}$ ,<sup>[42]</sup> and thiophenes.<sup>[66]</sup> Addition products to the double bond as well as substitution products are observed. Roberts showed in 1964 that the thermal reaction of  $(\text{F}_3\text{CO})_2$  with stoichiometric amounts of  $\text{F}_2\text{C}=\text{CFCF}_3$  leads to a series of homo-oligomers  $\text{F}_3\text{CO}(\text{C}_3\text{F}_6)_n\text{OCF}_3$ , with  $n = 2, 3, 4$ . With excess propene, the only product obtained is

$F_3CO(C_3F_6)_4OCF_3$  [Equation (14)].<sup>[49]</sup> In a kinetic study by Descamps and Forst from 1975 the authors investigated the thermal decomposition of  $(F_3CO)_2$  in the presence of  $(FSO_2O)_2$  as a radical trapping agent, yielding trifluoromethyl peroxyfluorosulfonate,  $F_3COOSO_2F$ , as the only product [Equation (15)].<sup>[67]</sup>

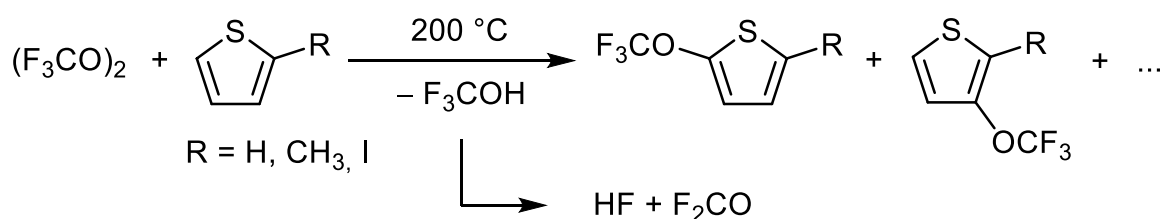


In 1976, Toy and Stringham showed that both perfluorinated peroxides  $(F_3CO)_2$  and  $[(F_3C)_3CO]_2$  react during irradiation with the perfluorinated cycloolefins  $c\text{-C}_5\text{F}_8$  and  $c\text{-C}_6\text{F}_{10}$ , as shown in Scheme 1.11.<sup>[42]</sup> In the first step of the radical chain mechanism, the initially formed  $R^FO^\bullet$  adds to the double bond of a cycloolefin. The subsequent dimerization of the perfluoroalkoxycycloalkyl radical is observed in the reaction with  $(F_3CO)_2$  (Scheme 1.11a), while a second  $R^FO^\bullet$  radical adds to the perfluoroalkoxycycloalkyl radical yielding di-*tert*-butoxycycloalkanes in the reaction with the bulkier  $[(F_3C)_3CO]_2$  (Scheme 1.11b). The different reaction behavior can be rationalized by the increased steric demand of  $(F_3C)_3CO^\bullet$  in comparison with  $F_3CO^\bullet$ , which decreases the tendency of dimerization of the perfluoroalkoxycycloalkyl radicals. Furthermore, the lifetime of  $(F_3C)_3CO^\bullet$  at  $-20\text{ }^\circ\text{C}$  is superior in comparison with  $F_3CO^\bullet$  radicals, which is in a reverse order to their thermal stability.<sup>[42]</sup>



**Scheme 1.11.** Irradiation of the perfluorinated peroxides  $(F_3CO)_2$  and  $[(F_3C)_3CO]_2$ , respectively, at  $-20\text{ }^\circ\text{C}$  in the presence of the perfluorocycloolefins,  $c\text{-C}_5\text{F}_8$  ( $n = 3$ ) or  $c\text{-C}_6\text{F}_{10}$  ( $n = 4$ ). In the case of  $(F_3CO)_2$ , the perfluoroalkoxycycloalkyl radical dimerizes (path a), while the reaction with  $[(F_3C)_3CO]_2$  yields perfluoro di-*tert*-butoxycycloalkanes (path b) in 50 to 70%.

These early studies prove that perfluorinated peroxides,  $(R^F O)_2$ , are suitable precursors for the transfer of a perfluoroalkoxy group,  $R^F O$ . This was later adopted by Peláez and Argüello in 2010, who reacted  $(F_3CO)_2$  with 2-substituted thiophenes by co-thermolysis in the gas phase, as shown in Scheme 1.12, to form mono-substituted thiophenes and trifluoromethanol,  $F_3COH$ .<sup>[66]</sup> This decomposes further to form hydrogen fluoride, HF, and  $F_2CO$ . The yields of the desired mono-substituted thiophenes are poor ( $R = H$ , 9%;  $R = CH_3$ , 22%) to moderate ( $R = I$ , 67%). The formation of these main products is accompanied by a variety of several regioisomers, two times substituted thiophenes, and polymers. Either a free-radical mechanism involving  $F_3CO^\bullet$  radicals, or an electron transfer mechanism from the substrate to  $(F_3CO)_2$ , giving a pair of a radical cation and a radical anion was postulated.<sup>[66]</sup> This “*new ‘green’ process*”<sup>[66]</sup> enables the introduction of  $F_3CO$ -groups to olefins with a great atom economy, compared with established chlorine-fluorine-exchange reactions in HF,<sup>[68]</sup> and without the use of mediating transition metals as palladium and silver.<sup>[69]</sup> Apart from the sparsely investigated thermal reactivity and photochemistry towards olefins, properties of such bulky perfluorinated dialkylperoxides  $(R^F O)_2$  remain largely unknown.

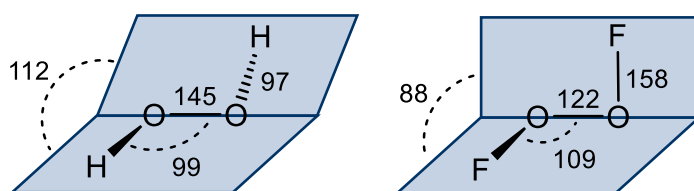


**Scheme 1.12.** Co-thermolysis of  $(F_3CO)_2$  with 2-substituted thiophenes.

## 1.2.3. Structures

The molecular structure of peroxides is mainly determined by the oxygen-oxygen bond length and the dihedral angle  $\Theta$  along ROOR. Both are generally influenced by the lone pair repulsion of the oxygen atoms, which results in a *gauche* structure, and steric effects of the substituents, favouring the *trans* structure, and electronic orbital effects.<sup>[5]</sup> The O–O bond length of hydrogen peroxide was determined by microwave spectroscopy (MW) to 145.3(7) pm (see Table 1.3. and Figure 1.3) and is in the range of an oxygen-oxygen single bond (149 pm, Table 1.1). At  $\Theta = 112^\circ$ , the Coulomb repulsion between the lone pairs at the oxygen atoms is lowered, which results in the *gauche* conformation or skew structure of (HO)<sub>2</sub>, as shown in Figure 1.3. In the solid state,  $\Theta$  is compressed to 90.2(3)° by strong intramolecular hydrogen bonding while the O–O bond length [145.3(4) pm] is unaffected.<sup>[70]</sup>

The molecular structure of its fluorinated counterpart, (FO)<sub>2</sub>, was determined in the solid state<sup>[28]</sup> as well as in the gas phase.<sup>[71]</sup> The structures show significantly elongated O–F bonds [solid: 161.8(2) pm<sup>[28]</sup>, gas: 157.5(3) pm<sup>[71]</sup>], e.g. compared with F<sub>2</sub>O (gas: 140.9 pm<sup>[72]</sup>) or HOF (solid: 144.2 pm<sup>[73]</sup>). The unusual short O–O bond length in (FO)<sub>2</sub> [solid: 118.6(2) pm<sup>[28]</sup>, gas: 121.7(3) pm<sup>[71]</sup>] along the peroxide unit (Figure 1.3 and Table 1.3) is more comparable to the bond length in molecular O<sub>2</sub> and is based on a



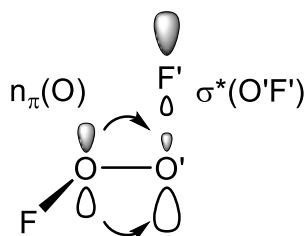
**Figure 1.3.** Molecular structures of (HO)<sub>2</sub> and (FO)<sub>2</sub> in the gas phase (bond lengths in pm and angles in °).

**Table 1.3.** Structure parameters of (HO)<sub>2</sub> and (FO)<sub>2</sub> (bond lengths  $d$  in pm and angles  $\angle$  and  $\Theta$  in °).

	(HO) <sub>2</sub>		(FO) <sub>2</sub>	
	MW <sup>[74,75]</sup>	CCSD(T) <sup>[75]</sup>	MW <sup>[71]</sup>	CCSD(T) <sup>[76]</sup>
$d(\text{OO})$	145.2(5)	145.3	121.7(3)	122.8
$d(\text{XO})$	96.5 <sup>[a]</sup>	96.3	157.5(3)	153.9
$\angle(\text{XOO})$	99.4(1)	99.9	109.3(3)	108.6
$\Theta(\text{XOOX})$	112(1) <sup>[12]</sup>	112.5	87.5(3)	87.7

[a] Assumed bond length.

large orbital interaction of the two lone pairs  $n_{\pi}(\text{O})$  and  $n_{\pi}(\text{O}')$  and the opposite antiperiplanar  $\sigma^*(\text{O}'\text{F}')$  and  $\sigma^*(\text{OF})$ ,<sup>[12]</sup> respectively, as shown in Figure 1.4. The sum of this orbital interactions in  $(\text{FO})_2$  was calculated to  $578 \text{ kJ mol}^{-1}$  [MP2/6-31G(d')].<sup>[12]</sup> This raises the O–O bond order with simultaneous shortening of the O–F connectivity. The interaction maximizes at  $\Theta \sim 90^\circ$ , as it is found for the “*anomalous compound*”<sup>[77]</sup> in both, the gas phase and in the solid state [ $\Theta = 88.3(1)^\circ$ ]. In comparison, the corresponding orbital interaction for  $(\text{HO})_2$  amounts to  $20 \text{ kJ mol}^{-1}$  at its maximum between  $\Theta = 80^\circ$  to  $90^\circ$ , while the interaction is zero for the *trans*-structure.<sup>[12]</sup> Therefore, the present dihedral angle of  $112(1)^\circ$  in the skew molecule  $(\text{HO})_2$  is the compromise between the steric repulsion and the orbital interaction.<sup>[12]</sup>



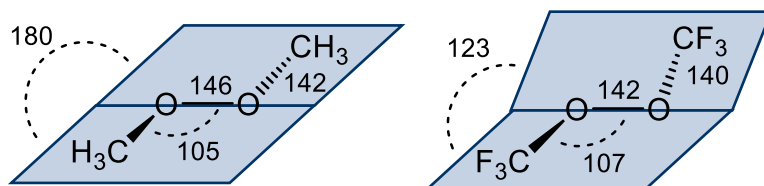
**Figure 1.4.** The anomeric effect in  $(\text{FO})_2$  – donation of electron density from  $n_{\pi}(\text{O})$  into the parallel orientated  $\sigma^*(\text{O}'\text{F}')$ .

These simple peroxides  $(\text{HO})_2$ ,<sup>[12,75]</sup> and  $(\text{FO})_2$ ,<sup>[76]</sup> respectively, were shown to have non-rigid structures with low *trans*- [( $\text{HO})_2$ :<sup>[74]</sup>  $385 \text{ cm}^{-1} = 4.6 \text{ kJ mol}^{-1}$ ;  $(\text{FO})_2$ :<sup>[76]</sup>  $7055 \text{ cm}^{-1} = 84.4 \text{ kJ mol}^{-1}$ ] and *cis*-barriers [( $\text{HO})_2$ :<sup>[74]</sup>  $2488 \text{ cm}^{-1} = 29.7 \text{ kJ mol}^{-1}$ ;  $(\text{FO})_2$ :<sup>[76]</sup>  $9047 \text{ cm}^{-1} = 108.2 \text{ kJ mol}^{-1}$ ]. The barriers are higher in the case of  $(\text{FO})_2$  due to enhanced orbital interaction with a resulting partial double bond character of the peroxide unit, but still low for the rotation along  $\Theta$ , resulting in a very flat energy potential for both peroxides. Hence, calculated minimum structures of such non-rigid molecules may differ significantly from the one obtained by experiment, but their long-standing contradiction was solved for  $(\text{HO})_2$  and  $(\text{FO})_2$  by modelling vibrationally averaged structures for the calculations.<sup>[75,76]</sup>

The experimental determination of the molecular structures in the gas phase of the methyl substituted dialkyl peroxide  $(\text{H}_3\text{CO})_2$  and its fluorinated counterpart  $(\text{F}_3\text{CO})_2$  suffers from similar flat energy potentials for the rotation along the dihedral angle  $\Theta$ . For  $(\text{H}_3\text{CO})_2$ , the variation within  $\pm 60^\circ$  around the calculated *trans*-minimum structure at a dihedral angle of  $\Theta = 180^\circ$  is less than  $100 \text{ cm}^{-1}$  ( $1.2 \text{ kJ mol}^{-1}$ ).<sup>[78]</sup> The *cis*-barrier was calculated to  $4058 \text{ cm}^{-1}$  ( $48.5 \text{ kJ mol}^{-1}$ ) at the CCSD(T)/aug-cc-pVTZ level.<sup>[78]</sup> Experimental GED data from 1984 by Haas and Oberhammer<sup>[79]</sup> has been

reinterpreted in 2017 by Ferchichi, Derbel and co-workers,<sup>[78]</sup> taking into account the vibrationally averaged structures for the model. This results in an O–O bond length of 145.7(1.2) pm and a dihedral angle of  $\Theta = 180.0^\circ$ , which is in excellent agreement with the calculations [ $d(\text{OO}) = 146.9$  pm,  $\Theta = 180.0^\circ$ ] at CCSD(T)/aug-cc-pVTZ level (Figure 1.5 and Table 1.4).

For  $(\text{F}_3\text{CO})_2$ , GED reveals an oxygen-oxygen bond length of 141.9(2.0) pm, see Figure 1.5.<sup>[80]</sup> This is approximately 4 pm shorter than that of the non-fluorinated derivative due to the electron withdrawing effects of the  $\text{CF}_3$  groups and the decreased lone pair electron repulsion of the oxygen atoms. Calculations at B3LYP/6-311G(d) level slightly overestimate the bond length (144.9 pm, Table 1.4). The dihedral angle along the COOC backbone was experimentally determined to  $\Theta = 123.3(4.0)^\circ$ , which agrees well with the calculations ( $124.0^\circ$ ). The *cis*-barrier of  $(\text{F}_3\text{CO})_2$  is assumed to be about  $80 \text{ kJ mol}^{-1}$  by cautious comparison with that of the structural related fluoro-peroxytrifluoromethane,  $\text{F}_3\text{COOF}$ ,<sup>[77,80]</sup> and therefore approximately twice the magnitude of  $(\text{H}_3\text{CO})_2$  ( $48.5 \text{ kJ mol}^{-1}$ ). The high barrier can possibly be rationalized by unfavourable F–F interactions enhanced by the torsion of  $(\text{F}_3\text{CO})_2$  along the O–O



**Figure 1.5.** Molecular structures of  $(\text{H}_3\text{CO})_2$  and  $(\text{F}_3\text{CO})_2$  in the gas phase (bond lengths in pm and angles in  $^\circ$ ).

**Table 1.4.** Structural parameters of dialkyl peroxides,  $(\text{R}^{(\text{F})}\text{O})_2$  (bond lengths  $d$  in pm and angles  $\angle$  and  $\Theta$  in  $^\circ$ ).

	$(\text{H}_3\text{CO})_2$		$(\text{F}_3\text{CO})_2$		$[(\text{H}_3\text{C})_3\text{CO}]_2$	
	GED <sup>[79]</sup>	CCSD(T) <sup>[a]</sup>	GED <sup>[80]</sup>	B3LYP <sup>[b]</sup>	GED <sup>[81]</sup>	XRD <sup>[82]</sup>
$d(\text{OO})$	145.7(1.2)	146.9	141.9(2.0)	144.9	148.0 <sup>[c]</sup>	147.8(3)
$d(\text{CO})$	142.0(7)	141.2	139.9(9)	139.0	146.0(9)	143.9(4)
$\angle(\text{COO})$	105.2(5)	103.7	107.2(1.2)	107.0	103.9(1.2)	106.7(2)
$\Theta(\text{COOC})$	180.0 <sup>[d]</sup>	180.0	123.3(4.0)	124.0	165.8(2.4)	164.0(4)

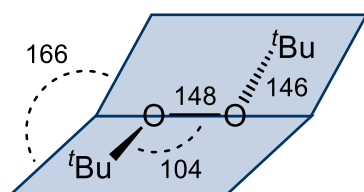
[a] CCSD(T)/aug-cc-pVTZ, ref. [78]. [b] B3LYP/6-311G(d), ref. [83]. [c] Fixed value.

[d] Reinterpreted, ref. [78].



bond, resulting in the *gauche*-arrangement of substituents. This is due to steric reasons. First, the increased van der Waals radius of F (147 pm<sup>[84]</sup>) in comparison with H (110 pm<sup>[84]</sup>) results in an increase of the *cis*-barrier of (F<sub>3</sub>CO)<sub>2</sub> (62.6 kJ mol<sup>-1</sup>) compared with (H<sub>3</sub>CO)<sub>2</sub> [47.0 kJ mol<sup>-1</sup>, B3LYP/6-31G(d,p)].<sup>[63]</sup> Second, steric repulsion of the trifluoromethyl groups of (F<sub>3</sub>CO)<sub>2</sub> is enabled by the relatively short O–O bond length of 142 pm.<sup>[80]</sup> The heavier F<sub>3</sub>C-substituted chalcogene derivatives have longer X–X distances (X = S: 203 pm, X = Te: 267 pm).<sup>[83]</sup> Therefore,  $\Theta$  along CXXC diminishes from 104° (X = S) to 88° (X = Te).<sup>[83]</sup> Furthermore, strong orbital interactions  $n_{\pi}(\text{O}) \rightarrow \sigma^*(\text{O}'\text{C}')$  favour  $\Theta = 90^\circ$ . They enforce due to the electron withdrawing effects of fluorine from 2.1 kJ mol<sup>-1</sup> for (H<sub>3</sub>CO)<sub>2</sub> to 4.5 kJ mol<sup>-1</sup> for (F<sub>3</sub>CO)<sub>2</sub>.<sup>[63]</sup> Accordingly, the dihedral angle of (F<sub>3</sub>CO)<sub>2</sub> is drastically enlarged by unfavourable F–F interactions due to the short bond length of the peroxide unit.

The structure of [(H<sub>3</sub>C)<sub>3</sub>CO]<sub>2</sub> was studied in both, the gas phase by GED<sup>[81]</sup> and in solid state by XRD.<sup>[82]</sup> The obtained dihedral angle  $\Theta = 165.8(2.4)^\circ$  in the gas phase (Figure 1.6 and Table 1.4) is not conclusive in comparison with the calculated equilibrium structure and could correspond either to a potential with large-amplitude torsional vibration, or a double minimum potential with a very low *trans*-barrier.<sup>[12]</sup> Calculations at MP2/6-31G(2d) level<sup>[63]</sup> reveal a value for this barrier of 1.03 kJ mol<sup>-1</sup>, favouring the thesis of a double minimum potential. Furthermore, the dipole moment [ $\mu = 0.89(3)$  D] indicates a dihedral angle of  $\Theta = 126^\circ$ .<sup>[85]</sup> The experiments in the gas phase and solid state reveal a skew structure of [(H<sub>3</sub>C)<sub>3</sub>CO]<sub>2</sub> with C<sub>2</sub> symmetry. In the solid state, the O–O bond length is 147.8(3) pm, slightly larger than that of its smaller homologue (H<sub>3</sub>CO)<sub>2</sub> [145.7(1.2) pm, Table 1.4]. This length could not be determined by GED and was fixed to 148 pm. Apparently, steric repulsion between bulky *tert*-butyl groups dominates the molecular structure of [(H<sub>3</sub>C)<sub>3</sub>CO]<sub>2</sub>, which leads to the increase of  $d(\text{OO})$  and the dihedral angle  $\Theta$ .<sup>[63]</sup>



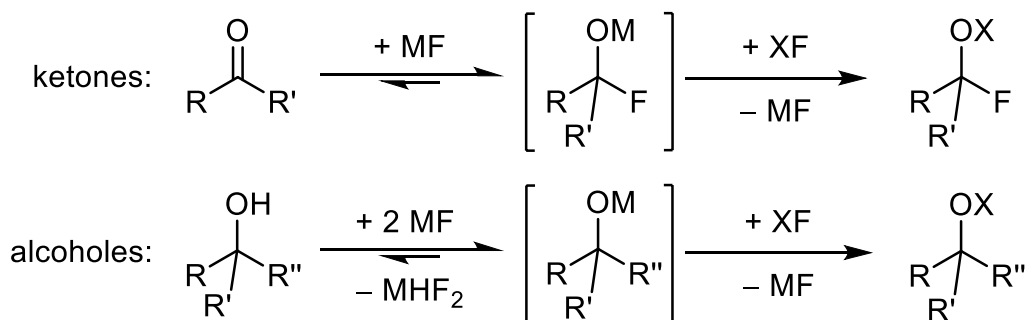
**Figure 1.6.** Molecular structure of [(H<sub>3</sub>C)<sub>3</sub>CO]<sub>2</sub> in the gas phase (bond lengths in pm and angles in °).

### 1.3. Hypohalites

Photolysis of perfluoroalkyl hypohalites,  $R^F OX$  ( $X = F, Cl$ ), lead to the abstraction of the halogen radical,  $X^\cdot$ . Subsequent combination of the remaining alkoxy radicals  $R^F O^\cdot$ , yields dialkyl peroxides,  $R^F OOR^F$  with  $R^F = F_3C, (F_3C)_3C$ .<sup>[40,43]</sup> This designates the compound class of perfluoroalkyl hypofluorites,  $R^F OF$ , and hypochlorites,  $R^F OCl$ , as convenient precursors for the synthesis of peroxides  $R^F OOR^F$ .

Hypohalites,  $ROX$  ( $X = Cl, Br$  or  $I$ ), are compounds with the halogen  $X$  in the oxidation state  $+I$ .<sup>[2]</sup> For  $X = F$  the oxidation state is  $-I$ . Hypohalites derive from hypohalite acids,  $HOX$ , or their conjugated bases, respectively. The disproportionation of the halogen,  $X_2$ , in water,  $H_2O$ , is in equilibrium with the corresponding hypohalite acid,  $HOX$ .<sup>[2]</sup> Hypofluorous acid,  $HOF$ , first described in 1927 by Lebeau and Damiens, is obtained electrochemically or by the circulation of  $F_2$  over ice water at  $-50^\circ C$ , besides  $O_2$ ,  $OF_2$  and traces of  $H_2O_2$ .<sup>[86]</sup> The two-step mechanism of the formation of this strong oxidizing compound was later investigated with isotopic labelling by Appelman and Jache.<sup>[86]</sup> Rozen tamed and utilized the oxidizing potential by performing the fluorination of water in acetonitrile, leading to the complex  $HOF \cdot CH_3CN$  with an increased lifetime of about 4 h at ice bath temperature.<sup>[87]</sup> This hypofluorite complex is widely used as an oxidation reagent, e.g. for stereospecific epoxidation reactions.<sup>[88]</sup>

The first perfluoroalkyl hypofluorite, trifluoromethyl hypofluorite,  $F_3COF$ , was obtained by Cady and Kellogg in 1948 by the  $AgF_2$ -catalyzed direct fluorination of carbon monoxide or gaseous methanol,  $H_3COH$ .<sup>[89]</sup> In 1966 Ruff and Lustig developed an alternative synthesis route, which enables a wider range of accessible perfluoroalkyl hypofluorites.<sup>[90]</sup> The addition of a perfluoro ketone,  $RR'CO$  ( $R, R' = F, CF_3, C_2F_5$ ), to a metal fluoride,  $MF$  ( $M = K, Rb, Cs$ ), leads to the formation of the corresponding perfluoro alcoholate (Scheme 1.13). Subsequent fluorination at  $-78^\circ C$  yields the metal fluoride, together with the primary and secondary perfluoroalkyl hypofluorite, e.g.  $C_2F_5OF$ ,  $C_3F_7OF$  and  $(F_3C)_2FCOF$ . The metal fluoride acts as a catalyst. This reaction sequence was adopted in the following years by Anderson and co-workers and made the related compound class of perfluorinated hypochlorites available, e.g.  $F_3COCl$ ,  $C_2F_5OCl$  and  $(F_3C)_2CFOCl$ . Addition of chlorine monofluoride,  $ClF$ , to the previously formed perfluoro alcoholate then forms the corresponding hypochlorite [Scheme 1.13].<sup>[91,92]</sup> Analogously, nonafluoro-*tert*-butanol,  $HOC(CF_3)_3$ , reacts in the



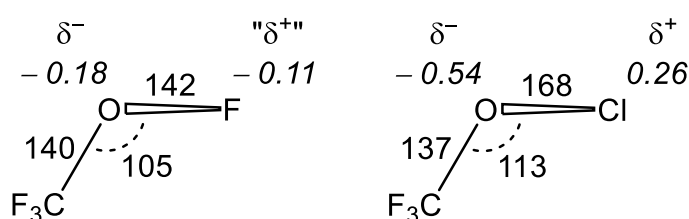
**Scheme 1.13.** Syntheses of perfluoroalkyl hypohalites  $\text{RR}'\text{R}''\text{COX}$  ( $\text{R}, \text{R}', \text{R}'' = \text{F}, \text{CF}_3, \text{C}_2\text{F}_5$ ;  $\text{X} = \text{F}, \text{Cl}$ ). The reaction of ketones ( $\text{RR}'\text{CO}$ , top) or tertiary alcohols ( $\text{RR}'\text{R}''\text{COH}$ , bottom) in the presence of MF ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ ) quantitatively yields the corresponding perfluoroalkyl alcoholate,  $\text{RR}'\text{R}''\text{COM}$ . Subsequent reaction with  $\text{F}_2$  leads to perfluoroalkyl hypofluorites,  $\text{RR}'\text{R}''\text{COF}$ , while the reaction with  $\text{ClF}$  yields perfluoroalkyl hypochlorites,  $\text{RR}'\text{R}''\text{COCl}$ .

presence of  $\text{CsF}$  with  $\text{F}_2$  to nonafluoro-*tert*-butyl hypofluorite,  $(\text{F}_3\text{C})_3\text{COF}$ ,<sup>[93]</sup> and with  $\text{ClF}$  to nonafluoro-*tert*-butyl hypochlorite,  $(\text{F}_3\text{C})_3\text{COCl}$ .<sup>[94]</sup> This extends the compound class to tertiary perfluorinated hypohalites.  $\text{CsF}$  traps the formed  $\text{HF}$ ,<sup>[95]</sup> as shown in Scheme 1.13.

Since then, a variety of hypohalites have been characterized, such as  $\text{F}_5\text{SOF}$ <sup>[96]</sup> and  $\text{F}_5\text{SOCl}$ <sup>[92]</sup>, and compounds with alkyl groups containing either chloride (e.g.  $\text{Cl}_3\text{CCF}_2\text{OF}$ )<sup>[93,97]</sup>, nitrogen (e.g.  $\text{NF}_2\text{CF}_2\text{CF}_2\text{OF}$ )<sup>[98]</sup>, sulfur (e.g.  $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OF}$ )<sup>[99]</sup>, and hydrogen (e.g.  $\text{H}_3\text{COF}$ )<sup>[100]</sup>. Alternatively, trifluoromethyl hypochlorite,  $\text{F}_3\text{COCl}$ , can be synthesized in a continuous process<sup>[101]</sup> or is obtained by the reaction of oxygen dichloride,  $\text{Cl}_2\text{O}$ , with carbonyl fluoride,  $\text{F}_2\text{CO}$ , in the presence of  $\text{CsF}$ , whereas the analog reaction of oxygen difluoride,  $\text{F}_2\text{O}$ , with  $\text{F}_2\text{CO}$  leads to  $\text{F}_3\text{COOF}$ .<sup>[92]</sup>

The trifluoromethyl hypohalites  $\text{F}_3\text{COF}$  and  $\text{F}_3\text{COCl}$ , seem closely related, but their properties and reactivities differ significantly.<sup>[102]</sup> This is due to the difference of electronegativities ( $\Delta\text{EN} = \text{EN}_\text{O} - \text{EN}_\text{X}$ ) of the oxygen atom and the corresponding halogen F ( $\Delta\text{EN} = -0.67$ ) and Cl ( $\Delta\text{EN} = 0.67$ ), respectively. Indeed, the weak O–F bond in  $\text{F}_3\text{COF}$  ( $184.2 \pm 3.3 \text{ kJ mol}^{-1}$ ,<sup>[39]</sup>  $\text{F}_3\text{CO}-\text{H}$ :<sup>[103]</sup>  $491.6 \pm 7.9 \text{ kJ mol}^{-1}$ ) is low polar ( $\mu = 0.30 \pm 0.02 \text{ D}$ )<sup>[104]</sup> and the hypofluorite atom was calculated to be a slightly negatively polarized [ $\sigma(\text{F}) = -0.11$ , B3LYP/6-311G\*],<sup>[105]</sup> see Figure 1.7 and Table 1.5. In contrast, the O–Cl bond in  $\text{F}_3\text{COCl}$  is slightly stronger ( $220.9 \pm 8.4 \text{ kJ mol}^{-1}$ )<sup>[106]</sup> and the positive net atomic charge  $\sigma$  of the hypochlorite atom in  $\text{F}_3\text{COCl}$  was shown by its

reaction with HCl, yielding  $F_3COH$  and  $Cl_2$ ,<sup>[107]</sup> and later calculated by natural population analysis (NPA) to 0.26 (B3LYP/6-31+G\*<sup>[105]</sup>). The O–F bond length of  $F_3COF$  in the gas phase [142.4(6) pm, see Figure 1.7 and Table 1.5] is comparable to that of  $F_2O$  (gas: 140.9 pm<sup>[72]</sup>) or  $HOF$  (solid: 144.2 pm<sup>[73]</sup>), while that of  $F_3COCl$  [167.9(3) pm] is elongated according to the increased ionic radius of the halogen. The bond angle  $\angle(COX)$  of  $F_3COF$  [104.8(6)°] is compressed in comparison with its chlorinated counterpart  $F_3COCl$  [112.9(5)°], see Figure 1.7 and Table 1.5, which is in consistency with Bents' rule.<sup>[108]</sup> While  $F_3COF$  is thermally stable up to 450 °C,<sup>[89]</sup>  $F_3COCl$  decomposes above 150 °C.<sup>[92]</sup>



**Figure 1.7.** Structural parameters (bond lengths in pm, angle in °) and polarization of the O–X bond with atomic charges  $\sigma$  in *italic numbers* [B3LYP/6-311G\*]<sup>[105]</sup> in trifluoromethyl hypohalites,  $F_3COX$  ( $X = F, Cl$ ).

**Table 1.5.** Properties and structural parameters (bond lengths  $d$  in pm and angle  $\angle$  in °) of  $F_3COF$  and  $F_3COCl$  in the gas phase.

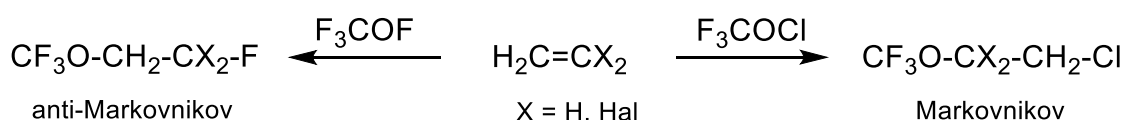
	$F_3COF$	$F_3COCl$
m.p. / b.p. [°C]	$<-215 / -95$ <sup>[89]</sup>	$-142 / -47$ <sup>[91]</sup>
BDE(OX) [kJ mol <sup>-1</sup> ]	$184.2 \pm 3.3$ <sup>[50]</sup>	$220.9 \pm 8.4$ <sup>[50]</sup>
$\sigma(O)$	$-0.18$ <sup>[105]</sup>	$-0.54$ <sup>[105]</sup>
$\sigma(X)$	$-0.11$ <sup>[105]</sup>	$0.26$ <sup>[105]</sup>
$d(OX)$ [pm]	$142.4(6)$ <sup>[109]</sup>	$167.9(3)$ <sup>[110]</sup>
$d(CO)$ [pm]	$139.5(6)$ <sup>[109]</sup>	$136.5(7)$ <sup>[110]</sup>
$\angle(COX)$ [°]	$104.8(6)$ <sup>[109]</sup>	$112.9(5)$ <sup>[110]</sup>

The low dissociation energy of the O–X bond facilitates the insertion of CO or sulfur dioxide, to form fluoroformates, e.g.  $F_3COC(O)F$ ,<sup>[111]</sup> and chloroformates,  $R^FOC(O)Cl$  ( $R^F =$  e.g.  $H_3C, Ph, F_3C, C_2F_5$ ),<sup>[40,112]</sup> and chlorosulfates,  $R^FOSO_2Cl$  ( $R^F =$  e.g.  $F_3CCH_2, (F_3C)_3C$ ),<sup>[94]</sup> respectively. The reactivity towards metals and elements was also studied. While  $F_3COF$  oxidizes mercury to dimercury difluoride,  $Hg_2F_2$ , [Equation (16)],<sup>[113]</sup> the

reaction of  $F_3COCl$  with mercury yields  $HgClF$  [Equation (19)].<sup>[114]</sup> In contrast, the bulkier nonafluoro-*tert*-butyl hypochlorite,  $(F_3C)_3COCl$ , undergoes oxidative addition in the presence of Hg to yield  $(F_3C)_3COHgCl$  [Equation (18)].<sup>[115]</sup> In the case of vanadyl trichloride, tellurium or bismuth, the reaction with the hypochlorite forms metal–oxygen bonds under the release of  $Cl_2$  [see Equations (19) to (21)].<sup>[116]</sup>

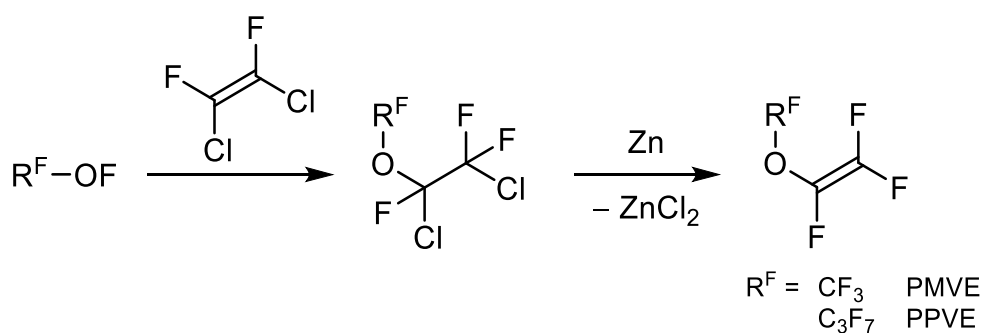


Trifluoromethyl hypohalites,  $F_3COX$  ( $X = F, Cl$ ), still provide a close relation to one another, since both are sources of an electrophilic halogen “ $X^+$ ” (compare to Figure 1.7).<sup>[117]</sup> The clean and selective addition of trifluoromethyl hypofluorite to organic steroids with olefinic double bonds was investigated by Hesse<sup>[118]</sup> and co-workers and later adopted by Rozen<sup>[119]</sup> and co-workers in the seventies of the last century. Nevertheless, the different reaction behavior of  $F_3COF$  and  $F_3COCl$  was pointed out by a study of Johri and DesMarteau from 1983 to emphasize their regio- and stereospecificity.<sup>[102]</sup> The addition of the hypohalites to numerous simple olefins,  $X_2C=CX_2$  ( $X, Y = \text{e.g. H, F, Cl}$ ), to form ethers, differs significantly. Since  $F_3COF$  reacts way faster and at lower temperatures than  $F_3COCl$ , it mainly yields anti-Markovnikov products in a free radical mechanism providing poor or no stereo- and a regioselectivity (Scheme 1.14). In contrast, the hypochlorite yields Markovnikov products by *syn*-addition. The relatively high stereoselectivity of  $F_3COCl$  is consistent with a polar electrophilic addition mechanism.<sup>[102]</sup>



**Scheme 1.14.** The addition of trifluoromethyl hypohalites to olefins,  $H_2C=CX_2$  ( $X = H, \text{Hal}$ ), mainly yields anti-Markovnikov products in the case of  $F_3COF$  and Markovnikov products for  $F_3COCl$ .

The ability of  $F_3COF$  to yield dialkyl ethers was adopted by the chemical industry<sup>[120]</sup> for the preparation of fluorinated synthetics as thermoplastic fluoropolymers and fluoroelastomers, like perfluoroalkoxy alkanes (PFA).<sup>[121,122]</sup> Trifluoromethyl hypofluorite,  $F_3COF$ , reacts with 1,2-dichloro-1,2-difluoroethylene,  $ClFC=CClF$ , to the corresponding dichlorinated ether (Scheme 1.15). The following reduction with zinc yields perfluoromethylvinylether (PMVE),  $F_3COCF=CF_2$ , which is a valuable fluorinated monomer.<sup>[121]</sup> Subsequent co-polymerization with tetrafluoroethylene,  $F_2C=CF_2$ , provides PFA. Heptafluoropropyl hypofluorite,  $n-C_3F_7OF$ , represents another industrial relevant compound in this reaction sequence for the analogue preparation of perfluoropropylvinylether (PPVE),  $C_3F_7OCF=CF_2$ .<sup>[121]</sup>



**Scheme 1.15.** Addition of  $R^FOF$  ( $R^F = CF_3, C_3F_7$ ) to  $ClFC=CClF$  with subsequent reduction with zinc yields perfluoromethylvinylether (PMVE) or perfluoropropylvinylether (PPVE).

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## 2. Objective

The discovery of perfluorinated dialkyl peroxides and their targeted syntheses led to a new class of compounds. Their unexpected stability provides great potential for applications in chemical syntheses, but their preparation exhibits difficulties and is often concerned as dangerous.

Aiming for alternative, safer and more convenient approaches to perfluorinated peroxides, a gentle syntheses of both, the hypohalites as their suitable precursors, and the peroxides themselves, is required. Hence, the purpose of this work is the development of feasible synthetic routes towards these classes of compounds. Since the available spectroscopic data for perfluorinated peroxides is deficient, receiving vibrational spectra and structural data is required.



### 3. Publications

#### 3.1. Perfluoro Alkyl Hypofluorites and Peroxides Revisited

Jan H. Nissen, Thomas Drews, Benjamin Schröder, Helmut Beckers, Simon Steinhauer, and Sebastian Riedel

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#### Author contributions

Jan H. Nissen designed the project, performed the experiments, with support of Thomas Drews, and the product characterization and wrote the publication. Benjamin Schröder did parts of the presented experiments during his internship supervised by Jan H. Nissen. Simon Steinhauer, Helmut Beckers and Sebastian Riedel supervised the project, provided scientific guidelines and suggestions and corrected this manuscript.



### 3.2. From hypochlorites to perfluorinated dialkyl peroxides

Jan H. Nissen, Lucas Wickemeyer, Tony Stüker, Simon Steinhauer, Helmut Beckers, and Sebastian Riedel

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#### **Author contributions**

Jan H. Nissen designed the project, performed the experiments and the product characterization and wrote the publication. Lucas Wickemeyer did parts of the presented experiments during his internship supervised by Jan H. Nissen. Tony Stüker contributed with TD-DFT calculations. Simon Steinhauer, Helmut Beckers and Sebastian Riedel supervised the project, provided scientific guidelines and suggestions and corrected this manuscript.



### 3.3. No Fear of Perfluorinated Peroxides

Jan H. Nissen, Tony Stüker, Thomas Drews, Simon Steinhauer, Helmut Beckers, and Sebastian Riedel

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#### Author contributions

Jan H. Nissen designed the project, performed the experiments, with support of Thomas Drews, and the product characterization and wrote the publication. Tony Stüker executed quantum-chemical calculations. Simon Steinhauer, Helmut Beckers and Sebastian Riedel supervised the project, provided scientific guidelines and suggestions and corrected this manuscript.

## 4. Summary

In this thesis, the convenient synthesis of perfluorinated alkyl hypofluorites,  $R^F\text{OF}$ , and hypochlorites,  $R^F\text{OCl}$ , was presented. Those hypohalites were shown to be suitable precursors for otherwise difficult to access perfluorinated dialkyl peroxides,  $R^F\text{OOR}^F$ . Their physical, chemical and structural properties were investigated.

Ketones or alcohols react with elemental fluorine in the presence of caesium fluoride to yield strong oxidizing hypofluorites. Their synthesis could be improved by the use of excess caesium fluoride, which dissipates local heat. The modified addition of fluorine in small portions at low temperatures provides a more secure and suitable synthetic route to this class of highly reactive compounds. The presented hypofluorites are stable at moderate temperatures and even the very volatile  $\text{F}_3\text{COF}$  can be handled in glass. When stored in steel vessels, no decomposition was observed after several months. Solely *tert*-pentyl hypofluorite decomposes fast at room temperature. Spectroscopic analysis of the obtained hypofluorites  $\text{F}_3\text{COF}$ ,  $\text{C}_2\text{F}_5\text{OF}$ ,  $(\text{F}_3\text{C})_2\text{FCOF}$ ,  $(\text{F}_3\text{C})_3\text{COF}$ , and  $(\text{C}_2\text{F}_5)(\text{F}_3\text{C})_2\text{COF}$  was performed and compared with quantum-chemical calculations. The characteristic O–F function of the perfluoroalkyl hypofluorites has unique spectroscopic properties. In their gas-phase IR spectra, the vibration mode of this bond shows a weak absorption in the region of 950 to 890  $\text{cm}^{-1}$ . In their  $^{19}\text{F}$  NMR spectra, the resonance of the fluorine atom of the hypofluorite groups is located at about +150 ppm.

The related perfluoroalkyl hypochlorites  $\text{F}_3\text{COCl}$ ,  $\text{C}_2\text{F}_5\text{OCl}$ ,  $(\text{F}_3\text{C})_2\text{FCOCl}$ ,  $(\text{F}_3\text{C})_3\text{COCl}$ , and  $(\text{C}_2\text{F}_5)(\text{F}_3\text{C})_2\text{COCl}$  were synthesized by the reaction of the corresponding ketone or alcohol with chlorine monofluoride in the presence of caesium fluoride. A full spectroscopic characterization of the hypochlorites including NMR, vibrational, and UV/Vis spectra was discussed, supported by quantum-chemical calculations at B3LYP and MP2 level. The O–Cl bond of the hypochlorites shows a very weak band in their gas-phase IR spectra at 790 to 780  $\text{cm}^{-1}$ , but they can easily be identified by UV/Vis spectroscopy due to their absorptions at about 250 nm and 350 nm, which are characteristic for this class of compounds.

A new synthetic approach towards perfluoro dialkyl peroxides,  $R^F\text{OOR}^F$ , from hypofluorites was developed. Hypofluorites react with fluorinated silver wool to form the corresponding peroxides. Investigations on the possible mechanism were carried out. It was also shown, that photolysis of hypochlorites provide a particularly suitable



access to these peroxides. Further understanding of the thermodynamics of this reaction was gained by quantum-chemical calculations. The synthesis of perfluoro dialkyl peroxides via hypofluorites requires relatively long reaction times of several days, whereas their provision by the irradiation of hypochlorites can be performed within one hour. Furthermore, the vapour pressure of hypochlorites is significantly decreased in comparison with the corresponding hypofluorites, which allows a comfortable handling in glass apparatuses. Therefore, hypochlorites represent the more convenient precursors for the synthesis of dialkyl peroxides.

The obtained tertiary perfluoro dialkyl peroxides bis(nonafluoro-*tert*-butyl) peroxide,  $[(F_3C)_3CO]_2$ , and bis(undecafluoro-*tert*-pentyl) peroxide,  $[(C_2F_5)(F_3C)_2CO]_2$ , were characterized by NMR, gas-phase IR, solid-state Raman and UV/Vis spectroscopy. They are liquid at room temperature and can easily be condensed or transferred with a syringe, which enables the usage in bulk as solvent or reactant. Their insensitivity to impact and friction and chemical resistance to acids and strong oxidizers as elemental halogens were discussed. It was shown by NMR experiments that  $[(F_3C)_3CO]_2$  dilutes elemental fluorine at room temperature. The peroxides are activated by UV irradiation to produce synthetically valuable perfluorinated alkoxy radicals,  $R^FO^\bullet$ , by homolytic oxygen–oxygen bond cleavage. The molecular structures of  $[(F_3C)_3CO]_2$  and  $[(C_2F_5)(F_3C)_2CO]_2$  in the solid state were obtained by in situ crystallization. The *trans* conformations along the peroxide backbones and the elongated oxygen–oxygen bonds are due to the steric demand of the perfluorinated alkyl groups.

In conclusion, this thesis includes the improved syntheses of perfluorinated alkyl hypohalites. This led to the extension of the hypofluorite and hypochlorite families to undecafluoro-*tert*-pentyl substituted hypohalites. From these hypohalites, new synthetic approaches to perfluorinated peroxides were developed. This class of compounds possesses an extraordinary physical and chemical resistance which enables the dissolution e.g. of elemental fluorine.

## 5. Publications and Conference Contributions

### 5.1. Published Manuscripts

J. H. Nissen, T. Stüker, T. Drews, S. Steinhauer, H. Beckers, S. Riedel, From hypochlorites to perfluorinated dialkyl peroxides, *J. Fluorine Chem.* **2020**, *230*, 109416.

J. H. Nissen, T. Drews, B. Schröder, H. Beckers, S. Steinhauer, S. Riedel, Perfluoro Alkyl Hypofluorites and Peroxides Revisited, *Chem. Eur. J.* **2019**, *25*, 14721–14727.

J. H. Nissen, T. Stüker, T. Drews, S. Steinhauer, H. Beckers, S. Riedel, No Fear of Perfluorinated Peroxides: Syntheses and Solid State Structures of Surprisingly Inert Perfluoroalkyl Peroxides, *Angew. Chem. Int. Ed.* **2019**, *58*, 3584–3588; *Angew. Chem.* **2019**, *131*, 3622–3626.

### 5.2. Published Patents

S. Hasenstab-Riedel, J. H. Nissen, H. Beckers, S. Steinhauer, T. Drews, H. Pernice, *Process For The Preparation Of Fluorinated Peroxides*, **2019**, WO2019207020A1.

J. Fabre, F. Hardinghaus, H. Pernice, S. Hasenstab-Riedel, H. Beckers, S. Steinhauer, J. H. Nissen, *Methods For Dielectrically Insulating Electrical Active Parts*, **2017**, WO2017191198A1.

### 5.3. Conference Contributions

08/2016	18 <sup>th</sup> European Symposium on Fluorine Chemistry Kiev, Ukraine	Guest
09/2016	17. Deutscher Fluortag Schmitten, Germany	Guest
07/2017	5. Tag der Anorganische Chemie Berlin, Germany	Organization
09/2017	GDCh-Wissenschaftsforum Chemie 2017 Berlin, Germany	Poster
07/2018	22 <sup>nd</sup> International Symposium on Fluorine Chemistry Oxford, England	Poster
09/2018	18. Deutscher Fluortag Schmitten, Germany	Oral
03/2019	Industry on Campus Berlin, Germany	Poster
08/2019	19 <sup>th</sup> European Symposium on Fluorine Chemistry Warsaw, Poland	Oral



## 7. Attachment

### 7.1. Synthesis of Perfluoro Methyl *tert*-Butyl Peroxide

Perfluoro methyl *tert*-butyl peroxide (PMTBP),  $F_3COOC(CF_3)_3$ , is obtained as a minor side-product in about 5% yield from the stoichiometric reaction of trifluoromethyl hypochlorite,  $F_3COCl$ , with silver nonafluoro-*tert*-butoxide,  $AgOC(CF_3)_3$ , at ice bath temperature. The peroxide is formed besides nonafluoro-*tert*-butyl carbonofluoridate,  $FC(O)OC(CF_3)_3$ , as shown in Scheme 7.1. After trap-to-trap distillation ( $-78\text{ }^\circ\text{C}$  /  $-120\text{ }^\circ\text{C}$  /  $-196\text{ }^\circ\text{C}$ ) of the crude product mixture, both compounds were obtained as colourless solids at  $-120\text{ }^\circ\text{C}$ . They were then added to an aqueous solution of sodium hydroxide and stirred at room temperature for 4 h. After subsequent hydrolysis of the fluoridate to form  $CO_2$  and  $HOC(CF_3)_3$ , the mixture can be separated by additional trap-to-trap distillation ( $-78\text{ }^\circ\text{C}$  /  $-120\text{ }^\circ\text{C}$  /  $-196\text{ }^\circ\text{C}$ ). The alcohol remains at  $-78\text{ }^\circ\text{C}$ , while  $CO_2$  passes the isolated PMTBP at  $-120\text{ }^\circ\text{C}$ . The powder X-Ray diffraction pattern of the remaining residue shows reflexes of the reactant  $AgOC(CF_3)_3$  and of the formed  $AgF$ , while reflexes for  $AgCl$  are not observed.

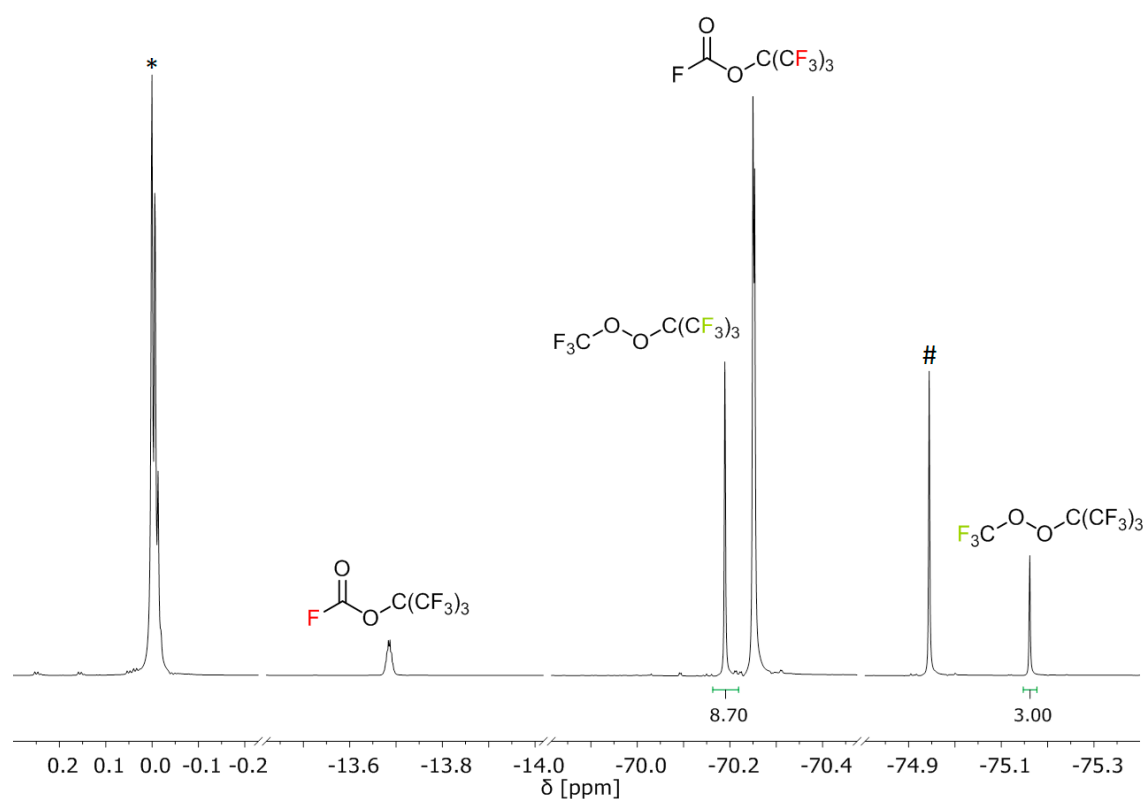
$^{19}\text{F}$  NMR (376.88 MHz,  $\text{CFCl}_3$ , external  $[\text{D}_6]\text{acetone}$ ,  $20.1\text{ }^\circ\text{C}$ ):  $\delta$  [ppm] =  $-70.2$  [s, 9F,  $\text{C}(\text{CF}_3)_3$ ],  $-75.2$  ppm (s, 3F,  $\text{CF}_3$ ).

IR (gas):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 1377 (m), 1320 (sh, s), 1303 (sh, s), 1287 (vs), 1260 (sh, s), 1248 (s), 1183 (s), 1152 (vs), 1123 (s), 1084 (m), 1071 (m), 998 (m), 982 (m), 957 (w) 846 (s), 733 (m), 711 (w).

APCI $^-$ :  $m/z$  = 470.9 (0.1%) [ $((\text{F}_3\text{C})_3\text{CO})_2\text{H}$ ] $^-$ , 234.9 (100.0%) [ $(\text{F}_3\text{C})_3\text{CO}$ ] $^-$ , 218.9 (9.0%) [ $(\text{F}_3\text{C})_3\text{C}$ ] $^-$ , 184.9 (9.0%) [ $(\text{F}_3\text{C})_2\text{FC}$ ] $^-$ , 85.0 (4.5%) [ $\text{F}_3\text{CO}$ ] $^-$ , 69.1 (1.2%) [ $\text{F}_3\text{C}$ ] $^-$ , 35.2 (0.6%) / 37.2 (0.3%) [ $\text{Cl}$ ] $^-$ .

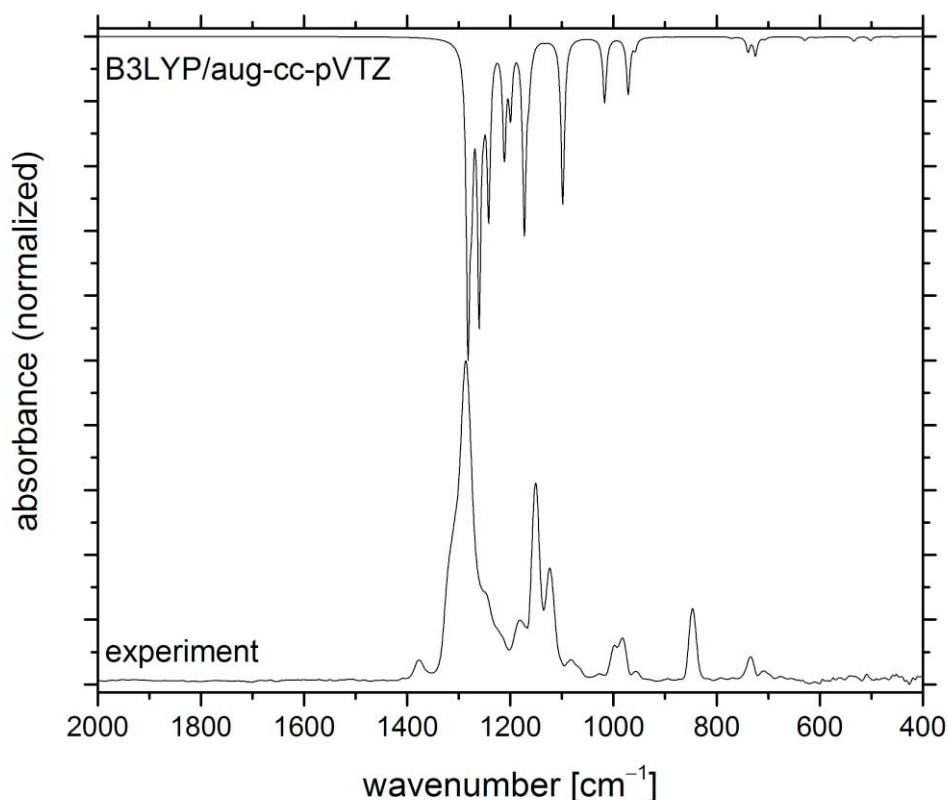


The  $^{19}\text{F}$  NMR spectrum (Figure 7.1) of the crude product mixture shows the signal of the single fluorine atom of  $\text{FC}(\text{O})\text{OC}(\text{CF}_3)_3$  at  $\delta = -13.7$  ppm as a decet. This is in discrepancy to the prior published chemical shift ( $\delta = -73.80$  ppm<sup>[123]</sup>) but in the region of the signals of acid fluorides  $\text{RC}(\text{O})\text{F}$ .<sup>[126]</sup> The coupling constant is  $^5J(\text{F},\text{F}) = 1.3$  Hz to the fluorine atoms of the *tert*-butyl group with a chemical shift of  $\delta = -70.3$  ppm. The singlet at  $\delta = -74.9$  ppm shows the resonance of the fluorine atoms of nonafluoro-*tert*-butanol due to hydrolysis of the silver salt. The fluorine atoms of the trifluoromethyl and nonafluoro-*tert*-butyl group of PMTBP,  $\text{F}_3\text{COOC}(\text{CF}_3)_3$ , are represented by the singlets at  $\delta = -70.2$  ppm and  $\delta = -75.2$  ppm, respectively, with an integral ratio of 9 to 3.



**Figure 7.1.**  $^{19}\text{F}$  NMR spectrum of a mixture of PMTBP,  $\text{FC}(\text{O})\text{OC}(\text{CF}_3)_3$  and  $\text{HOC}(\text{CF}_3)_3$  (#) [376.88 MHz,  $\text{CFCl}_3$  (\*), external  $[\text{D}_6]$ acetone, 20.1 °C].

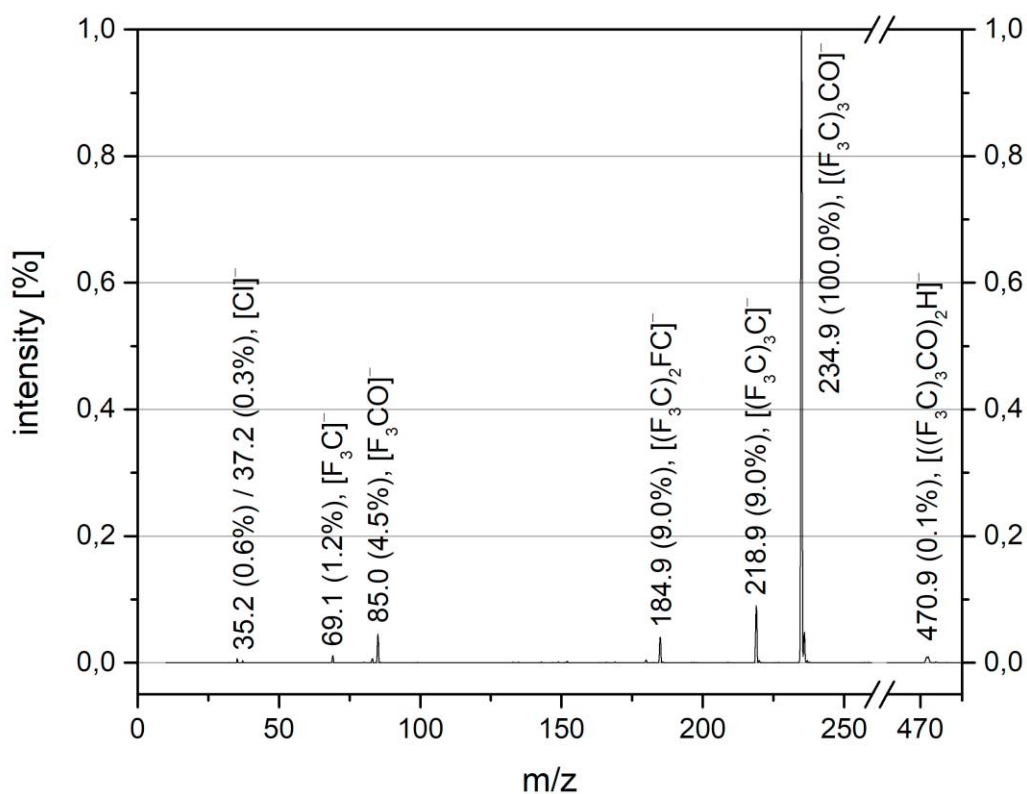
The gas-phase IR spectrum of the purified perfluoro methyl *tert*-butyl peroxide is shown in Figure 7.2 and compared with a calculated spectrum at B3LYP/aug-cc-pVTZ level (see Figure 7.4 and Table 7.1). Besides strong absorptions due to C–F vibration modes in the region from 1320 to 1152  $\text{cm}^{-1}$ , the bands at 1152 and 1124  $\text{cm}^{-1}$ , respectively, are tentatively assigned to the C–O vibrations of PMTBP (calc.: 1173  $\text{cm}^{-1}$ , 1098  $\text{cm}^{-1}$ ). The two bands at 998 and 982  $\text{cm}^{-1}$  in the gas-phase IR spectrum are due to C–C vibrations of the *tert*-butyl group of PMTBP and fit well to the calculated bands at 1017 and 971  $\text{cm}^{-1}$ . C–F deformation modes can be assigned to the absorptions at 738 and 711  $\text{cm}^{-1}$  (calc.: 784  $\text{cm}^{-1}$ , 725  $\text{cm}^{-1}$ ). The band at 846  $\text{cm}^{-1}$  may result from an unknown impurity. The characteristic O–O stretching mode of the asymmetric substituted peroxy group of PMTBP was calculated at 958  $\text{cm}^{-1}$  and can be assigned to the weak absorption at 957  $\text{cm}^{-1}$  in the gas-phase IR spectrum.



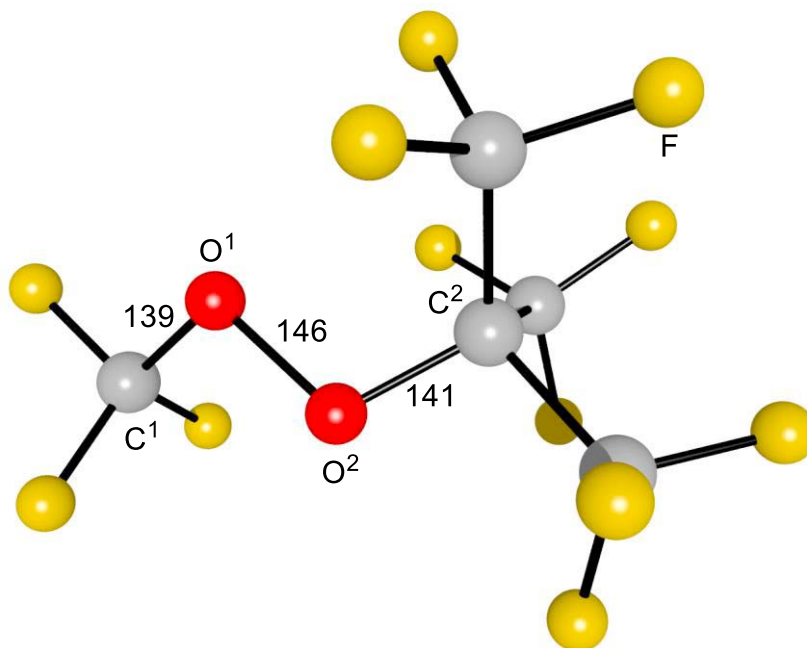
**Figure 7.2.** Gas-phase IR spectrum of  $\text{F}_3\text{COOC}(\text{CF}_3)_3$  (bottom, 1 mbar, 10 cm cell) in comparison with a calculated spectrum at B3LYP/aug-cc-pVTZ level (top).



In the APCI<sup>-</sup> mass spectrum of PMTBP (Figure 7.3) fragmentation of the peroxide is observed. The base peak at 234.9 m/z represents the [(F<sub>3</sub>C)<sub>3</sub>CO]<sup>-</sup> fragment. The peak 85.0 m/z is assigned to the corresponding [F<sub>3</sub>CO]<sup>-</sup> anion, while the molecular ion peak of F<sub>3</sub>COOC(CF<sub>3</sub>)<sub>3</sub> at 320.0 m/z is absent. Further fragmentation of the *tert*-butoxy group is observed at 218.9 and 184.9 m/z for [(F<sub>3</sub>C)<sub>3</sub>C]<sup>-</sup> and [(F<sub>3</sub>C)<sub>2</sub>FC]<sup>-</sup>, respectively. The small peak at 470.9 can be assigned to a proton bridged di-*tert*-butoxy anion [((F<sub>3</sub>C)<sub>3</sub>CO)<sub>2</sub>H]<sup>-</sup>. The [F<sub>3</sub>C]<sup>-</sup> anion is found at 69.1 m/z with a small intensity. The two peaks at 35.2 and 37.2 m/z (relative intensities: 3/1) are due to impurities of [Cl]<sup>-</sup>, as an artefact of prior measurements.



**Figure 7.3.** APCI mass spectrum of F<sub>3</sub>COOC(CF<sub>3</sub>)<sub>3</sub> in the negative mode.



**Figure 7.4.** Calculated minimum structure of  $F_3COOC(CF_3)_3$  at B3LYP/aug-cc-pVTZ level of theory [bond lengths in pm].  $\angle(C^1O^1O^2C^2) = 147^\circ$ .

**Table 7.1.** Coordinates of the computed structure of  $F_3COOC(CF_3)_3$  at B3LYP/aug-cc-pVTZ level of theory.

atom	x	y	z	atom	x	y	z
O	-6.15957	0.54719	-0.87720	F	-7.99229	1.15999	-1.80435
O	-4.77331	0.94342	-0.66526	F	-6.14103	1.75640	-2.77732
C	-6.74604	1.57027	-1.60642	F	-6.74982	2.72783	-0.95060
C	-4.33191	0.46639	0.58693	F	-2.24493	-0.27207	-0.33140
C	-2.76978	0.66720	0.45936	F	-2.18394	0.59325	1.65545
C	-4.66014	-1.06359	0.78732	F	-2.49491	1.85753	-0.07450
C	-4.89924	1.32864	1.77271	F	-4.56419	-1.71248	-0.37178
F	-4.38282	2.56196	1.73406	F	-5.89617	-1.23332	1.26553
F	-4.58924	0.77505	2.95128	F	-3.80456	-1.61589	1.65636
F	-6.22615	1.43958	1.69995				
				$E_{\text{total}} = -1539.0231887870 \text{ H}$			

## 7.2. Synthesis of Nonafluoro-*tert*-Butyl Hypobromite

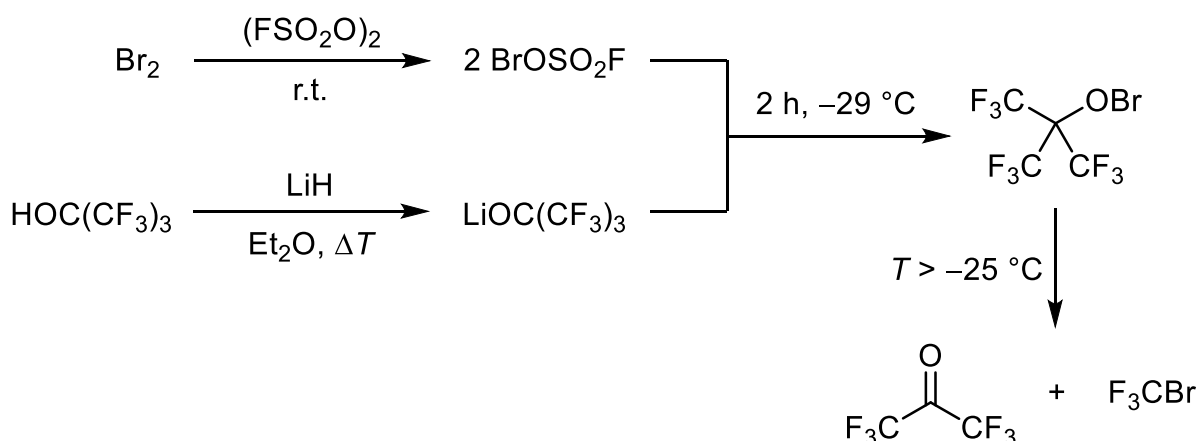
Nonafluoro-*tert*-butyl hypobromite,  $(\text{F}_3\text{C})_3\text{COBr}$ , was synthesized according to a protocol<sup>[127]</sup> from bromine(I) fluorosulfat,  $\text{BrOSO}_2\text{F}$ , and lithium nonafluoro-*tert*-butoxide,  $\text{LiOC}(\text{CF}_3)_3$ , at lower temperatures (Scheme 7.2). No spectroscopic data was given. The reactants  $\text{BrOSO}_2\text{F}$  and  $\text{LiOC}(\text{CF}_3)_3$ , respectively, were obtained by literature procedure.<sup>[124,125,128]</sup>

In a PFA-reactor, bromine fluorosulfat (0.3 g, 1.7 mmol) was added by condensation at liquid nitrogen temperature to solid lithium perfluoro-*tert*-butoxide (0.5 g, 2.0 mmol, 1.2 eq.). The mixture was warmed to  $-29\text{ }^\circ\text{C}$  and stirred for 2 h. The crude reaction was collected in an external trap cooled with liquid nitrogen and  $(\text{F}_3\text{C})_3\text{COBr}$  was separated via subsequent trap-to-trap distillation ( $-60\text{ }^\circ\text{C}$  /  $-95\text{ }^\circ\text{C}$  /  $-196\text{ }^\circ\text{C}$ ) at  $-95\text{ }^\circ\text{C}$  from its hydrolysis product  $\text{HOC}(\text{CF}_3)_3$  at  $-60\text{ }^\circ\text{C}$  and from its decomposition products  $(\text{F}_3\text{C})_2\text{CO}$  and  $\text{F}_3\text{CBr}$ , respectively, at  $-196\text{ }^\circ\text{C}$ .

$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100.51 MHz,  $\text{CFCl}_3$ , external  $[\text{D}_6]\text{acetone}$ ,  $-60\text{ }^\circ\text{C}$ ):  $\delta$  [ppm] = 118.8 [q,  $^1J(\text{F},\text{C}) = 295\text{ Hz}$ ,  $\text{CF}_3$ ], 82.0 [dec,  $^2J(\text{F},\text{C}) = 30\text{ Hz}$ ,  $\text{C}_q$ ].

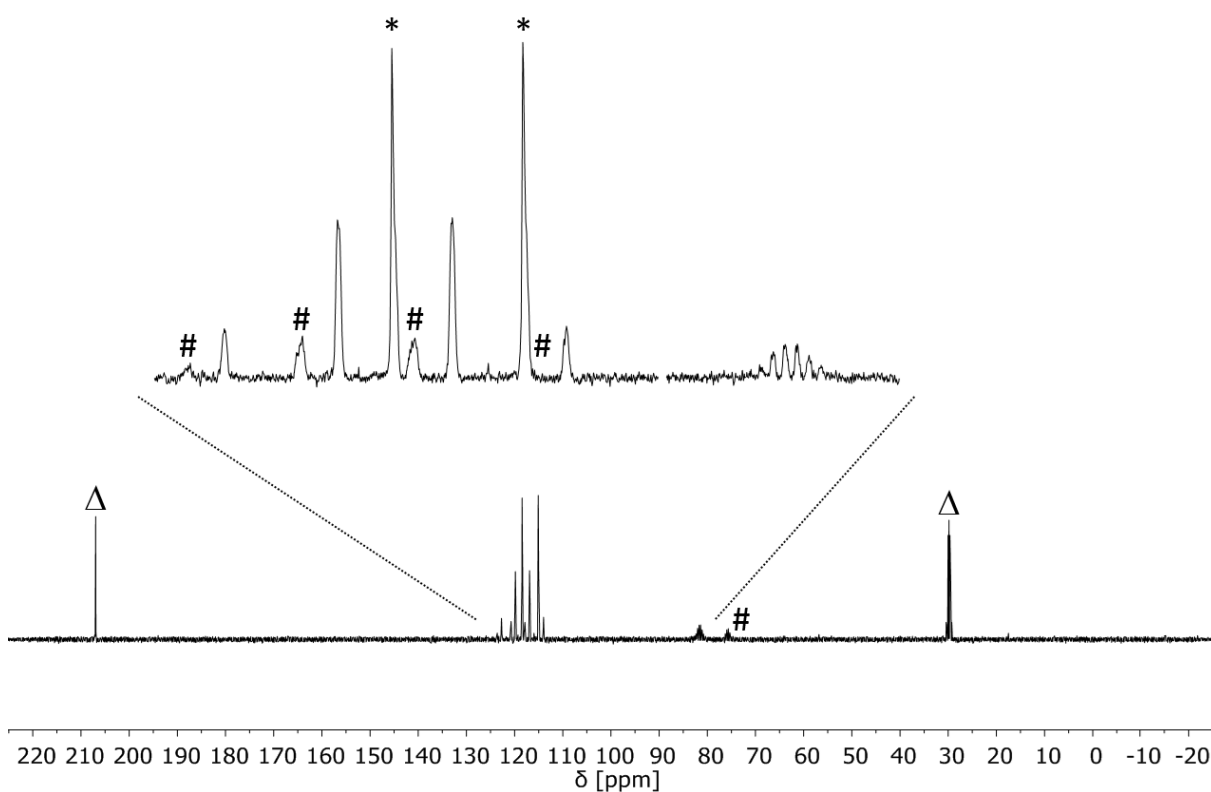
$^{19}\text{F}$  NMR (376.88 MHz,  $\text{CFCl}_3$ , external  $[\text{D}_6]\text{acetone}$ ,  $20.1\text{ }^\circ\text{C}$ ):  $\delta$  [ppm] =  $-71.3$  (s).

IR (gas):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 1300 (m), 1288 (vs), 1265 (m), 1229 (vw), 1209 (vw), 1191 (vw), 1109 (m), 997 (w), 980 (w), 741 (w), 730 (w), 708 (vw), 540 (vw).

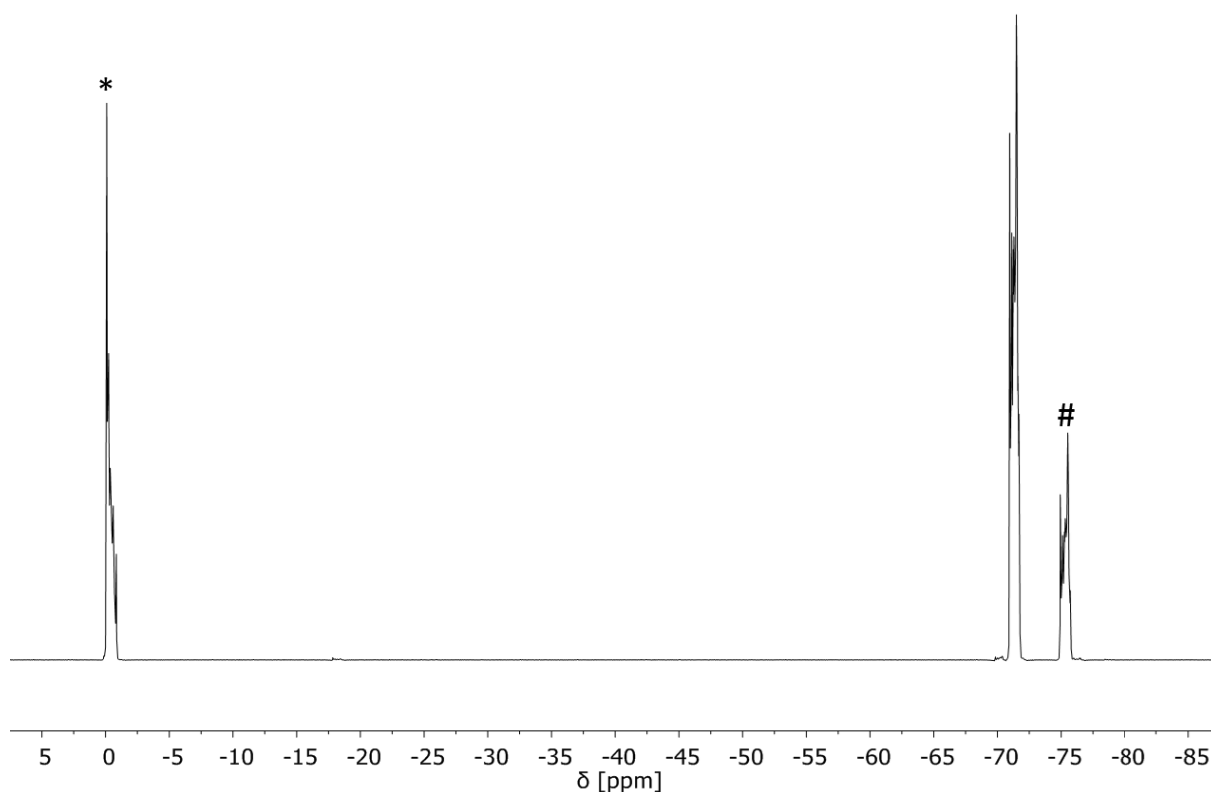


**Scheme 7.2.** Synopsis of the three-step synthesis of nonafluoro-*tert*-butyl hypobromite,  $(\text{F}_3\text{C})_3\text{COBr}$ , from bromine(I) fluorosulfat,  $\text{BrOSO}_2\text{F}$ , and lithium perfluoro-*tert*-butoxide,  $\text{LiOC}(\text{CF}_3)_3$ . The hypobromite decomposes at temperatures above  $-25\text{ }^\circ\text{C}$  to  $(\text{F}_3\text{C})_2\text{CO}$  and  $\text{F}_3\text{CBr}$ .

The low temperature  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectrum of nonafluoro-*tert*-butyl hypobromite,  $(\text{F}_3\text{C})_3\text{COBr}$  shows the resonance of the quaternary carbon atom at  $\delta = 82.0$  ppm (Figure 7.5) as a decet with a coupling constant of  $^2J(\text{F},\text{C}) = 30$  Hz. The quartet at  $\delta = 118.8$  ppm represent the carbon atoms of the  $\text{CF}_3$  groups with a coupling constant of  $^1J(\text{F},\text{C}) = 295$  Hz. Impurities of  $\text{HOC}(\text{CF}_3)_3$  as the hydrolysis product are annotated with #. In the low temperature  $^{19}\text{F}$  NMR spectrum (Figure 7.6) the resonance of the fluorine atoms of the hypobromite at  $\delta = -71.3$  ppm and the chemical shift of  $\text{HOC}(\text{CF}_3)_3$  appears at  $\delta = -75.3$  ppm. The supposed singlets in the  $^{19}\text{F}$  NMR spectrum are accompanied by artefacts with poor resolution.

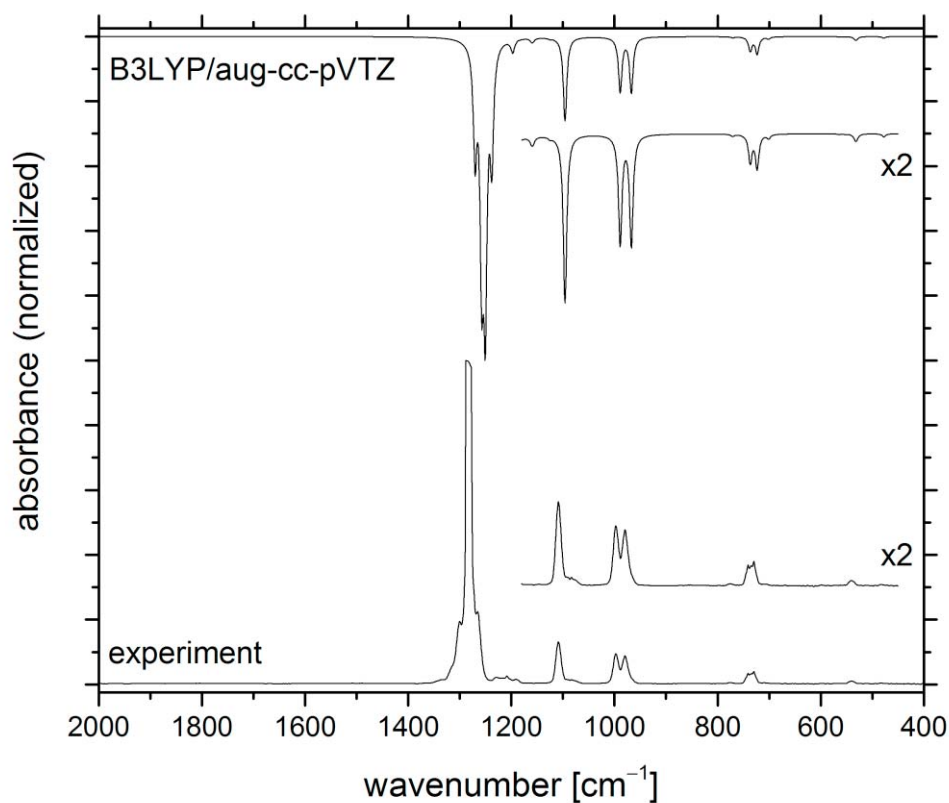


**Figure 7.5.**  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectrum of  $(\text{F}_3\text{C})_3\text{COBr}$  with impurities of  $\text{HOC}(\text{CF}_3)_3$  (#) (100.51 MHz,  $\text{CFCl}_3$  [\*], external  $[\text{D}_6]\text{acetone}$  [ $\Delta$ ],  $-60$  °C).

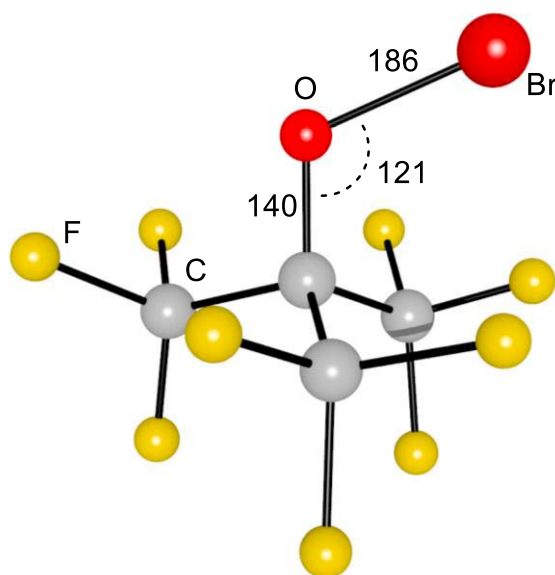


**Figure 7.6.**  $^{19}\text{F}$  NMR spectrum of  $(\text{F}_3\text{C})_3\text{COBr}$  with impurities of  $\text{HOC}(\text{CF}_3)_3$  (#) (376.88 MHz,  $\text{CFCl}_3$  [\*], external  $[\text{D}_6]\text{acetone}$ ,  $-60\text{ }^\circ\text{C}$ ).

The IR spectrum of  $(\text{F}_3\text{C})_3\text{COBr}$  in the gas phase (Figure 7.7) is compared with a calculated spectrum at B3LYP/aug-cc-pVTZ level (see Figure 7.8 and Table 7.2). It shows strong absorptions in the C–F stretching region from  $1300$  to  $1250\text{ cm}^{-1}$ . The C–O stretching mode is assigned to the strong band at  $1109\text{ cm}^{-1}$  (calc.:  $1096\text{ cm}^{-1}$ ). Furthermore, C–C vibrations of the *tert*-butyl group appear at  $997$  and  $980\text{ cm}^{-1}$  (calc.:  $989$  and  $967\text{ cm}^{-1}$ ), accompanied by their corresponding deformation modes at  $775$ ,  $741$ ,  $730$  and  $540\text{ cm}^{-1}$  (calc.:  $771$ ,  $737$ ,  $723$ ,  $538\text{ cm}^{-1}$ ). The O–Br mode is assigned to the very weak absorption at  $708\text{ cm}^{-1}$  (calc.:  $701\text{ cm}^{-1}$ ).



**Figure 7.7.** Gas-phase IR spectrum of  $(F_3C)_3COBr$  (bottom, 6 mbar, 10 cm cell) in comparison with a calculated spectrum at B3LYP/aug-cc-pVTZ level (top).



**Figure 7.8.** Calculated minimum structure of  $(F_3C)_3COBr$  at B3LYP/aug-cc-pVTZ level of theory (bond lengths in pm and angle in  $^\circ$ ).

**Table 7.2.** Coordinates of the computed structure of (F<sub>3</sub>C)<sub>3</sub>COBr at B3LYP/aug-cc-pVTZ level of theory.

atom	x	y	z	atom	x	y	z
C	-2.754117	2.768388	0.135600	F	-0.782166	2.919662	-1.209577
C	-1.181269	2.716915	0.047129	F	-0.711690	1.532307	0.453589
C	-3.220413	3.004884	1.618542	F	-0.625318	3.662576	0.816968
C	-3.351755	1.403405	-0.402236	F	-3.195136	0.424975	0.494530
O	-3.334288	3.694798	-0.742667	F	-2.734506	1.044246	-1.532546
F	-2.558655	2.211066	2.469522	F	-4.651696	1.526939	-0.663590
F	-4.529141	2.755758	1.739567	Br	-2.732218	5.450395	-0.823018
F	-3.014240	4.273015	1.988066	$E_{\text{total}} = -3700.2815198100$ H			

### 7.3. Synthesis of Bis(Nonafluoro-*tert*-Butyl) Carbonate

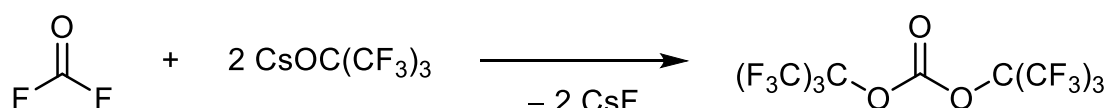
During the ambition to react trifluoromethyl hypofluorite,  $F_3COF$ , with thionyl tetrafluoride,  $SOF_4$ , to synthesize trifluoromethyl pentafluorosulfanyl peroxide,  $F_3COOSF_5$ , 10 mmol of each reactant was first irradiated with a Xe h.p. UV lamp for 2 h at  $-78\text{ }^\circ\text{C}$  in a quartz vessel. As no reaction was observed by IR spectroscopy, the mixture was then treated with fluorinated silver wool at r.t. for 1 d. Hence, besides small amounts of  $F_2CO$  as a decomposition product of  $F_3COF$ , the reactants still remained unchanged and were transferred to a stainless steel vessel containing 50 g CsF. After 12 h at r. t. the reaction mixture was collected in an external trap and subsequent trap-to-trap distillation ( $-78\text{ }^\circ\text{C} / -196\text{ }^\circ\text{C}$ ) yielded unreacted  $F_3COF$  together with  $F_2CO$ ,  $SOF_4$ , and small amounts of  $SiF_4$  at  $-196\text{ }^\circ\text{C}$ . Bis(nonafluoro-*tert*-butyl) carbonate (40 mg, 0.08 mmol) was isolated at  $-78\text{ }^\circ\text{C}$  as a colourless solid.

$^{13}\text{C} \{^{19}\text{F}\}$  DEPTQ NMR (100.7 MHz,  $CFCl_3$ , external  $[D_6]$ acetone,  $21.6\text{ }^\circ\text{C}$ ):  $\delta$  [ppm] = 142.8 (CO), 118.2 ( $CF_3$ ), 81.4 ( $C_q$ ).

$^{19}\text{F}$  NMR (376.88 MHz,  $CFCl_3$ , external  $[D_6]$ acetone,  $20.2\text{ }^\circ\text{C}$ ):  $\delta$  [ppm] =  $-70.1$  (s).

IR (gas):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 1899 (w), 1875 (sh, w), 1864 (s), 1821 (w), 1345 (sh, w), 1318 (sh, m), 1287 (vs), 1279 (vs), 1273 (vs), 1232 (w), 1190(m), 1178 (s), 1130 (w), 1097 (s), 1025 (s), 1003 (w), 989 (s), 798 (w), 773 (w), 753 (mw), 732 (m), 722 (sh, w), 701 (w), 525 (sh, w), 544 (w), 538 (w), 482 (w).

The steel vessel was frequently used for the synthesis of  $(F_3C)_3COF$  from the reaction of the corresponding alcohol,  $HOC(CF_3)_3$ , with  $F_2$ . It is assumed, that impurities of caesium nonafluoro-*tert*-butoxide,  $CsOC(CF_3)_3$ , reacted with  $F_2CO$  to form the carbonate (Scheme 7.3). It was prior described that the reaction of  $F_2CO$  with sodium<sup>[129]</sup> or potassium<sup>[123,130]</sup> nonafluoro-*tert*-butoxide,  $MOC(CF_3)_3$  ( $M = \text{Na}, \text{K}$ ), yields bis(nonafluoro-*tert*-butyl) carbonate,  $[(F_3C)_3CO]_2CO$ .

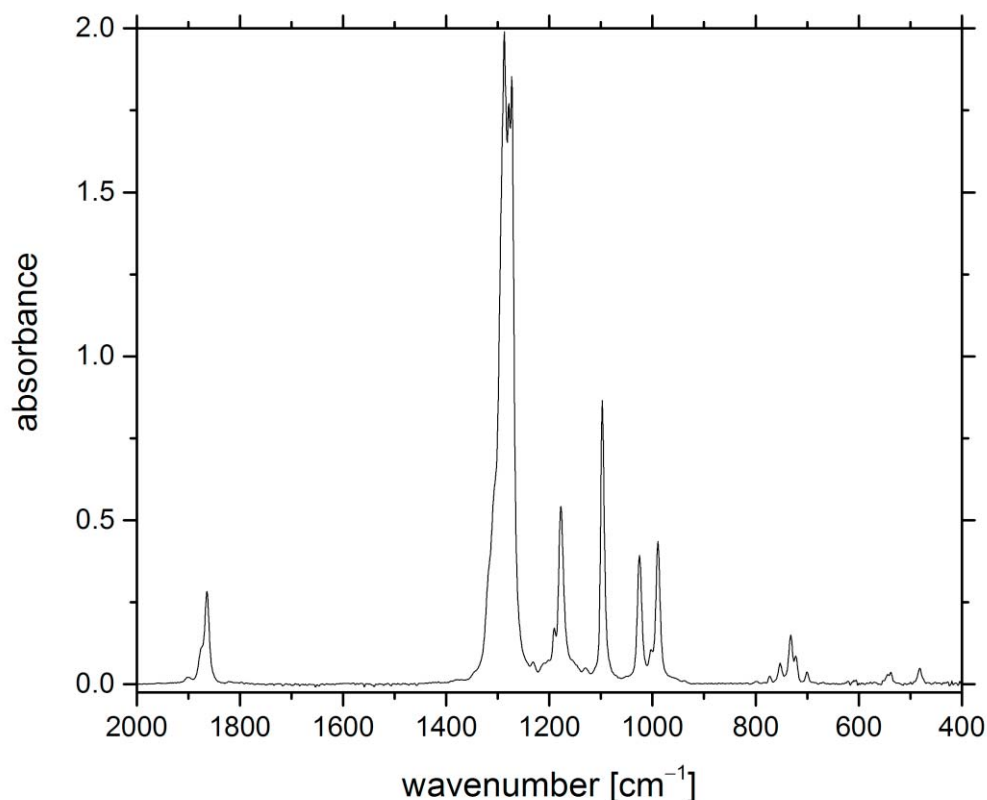


**Scheme 7.3.** Syntheses of bis(nonafluoro-*tert*-butyl) carbonate,  $[(F_3C)_3CO]_2CO$ , by the reaction of  $F_2CO$  with  $CsOC(CF_3)_3$  under elimination of caesium fluoride.



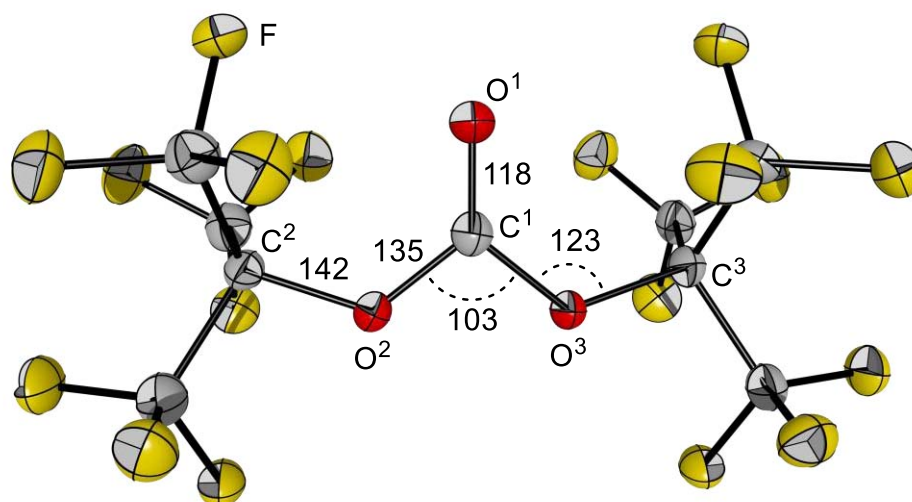
In the  $^{13}\text{C}$  NMR spectrum of  $[(\text{F}_3\text{C})_3\text{CO}]_2\text{CO}$ , the carbon atom of the carbonyl group resonates at low field at  $\delta = 142.8$  ppm, while the carbon atoms of the  $\text{CF}_3$  groups are represented by the peak at  $\delta = 118.2$  ppm. The signal at  $\delta = 81.4$  ppm is assigned to the two quaternary carbon atoms. The equivalent fluorine atoms resonate at  $\delta = -70.1$  ppm as a singlet in the  $^{19}\text{F}$  NMR spectrum (lit.:  $-70.20$  ppm<sup>[123]</sup>).

The IR spectrum of bis(nonafluoro-*tert*-butyl) carbonate in the gas phase (Figure 7.9) shows the characteristic carbonyl stretching mode at  $1864\text{ cm}^{-1}$ . Besides strong bands in region of  $1287$  to  $1273\text{ cm}^{-1}$  due to C–F vibrations, the absorptions at  $1178$  and  $1097\text{ cm}^{-1}$ , respectively, are tentatively assigned to the symmetric and antisymmetric C–O stretching modes. The C–C stretching modes are represented by the two absorptions at  $1025$  and  $989\text{ cm}^{-1}$ , while the corresponding deformation modes are located in the region from  $773$  to  $701\text{ cm}^{-1}$  and from  $552$  to  $539\text{ cm}^{-1}$ , in agreement with the literature.<sup>[123]</sup>



**Figure 7.9.** Gas-phase IR spectrum of  $[(\text{F}_3\text{C})_3\text{CO}]_2\text{CO}$  (1 mbar, 10 cm cell).

Solid bis(nonafluoro-*tert*-butyl) carbonate melts at about 42 °C and the boiling point is reached at about 110 °C.<sup>[131]</sup> Single crystals of  $[(F_3C)_3CO]_2CO$ , suitable for XRD analysis, were obtained by slow sublimation of the carbonate and the molecular structure is shown in Figure 7.10. The carbonate crystallizes in an orthorhombic system in the space group  $P2_12_12_1$  with  $C_s$  symmetry (Table 7.3). The C–O bond length of the carbonyl group is 117.9(5) pm. The sum of the angles at C<sup>1</sup> is 360° with a compressed angle  $\angle(O^2C^1O^3)$  of 103.2(3)°. The C<sup>1</sup>–O<sup>2/3</sup> distances are 1.348(5) and 1.350(5) pm, respectively. Both nonafluoro-*tert*-butyl groups are not congruently by  $C_2$  rotation along C<sup>1</sup>O<sup>1</sup>, represented by the dihedral angles  $\Theta$  along C<sup>2</sup>O<sup>2</sup>C<sup>1</sup>O<sup>3</sup> of  $-176.7(5)^\circ$  and along O<sup>2</sup>C<sup>1</sup>O<sup>3</sup>C<sup>3</sup> of  $174.8(5)^\circ$ , respectively.



**Figure 7.10.** Single-crystal molecular structure of  $[(F_3C)_3CO]_2CO$  in the solid state. Thermal ellipsoids are shown at 50% probability level. Selected bond lengths  $d$  and angles  $\angle$  and  $\Theta$ :  $d(C^1O^1) = 117.9(5)$  pm,  $d(C^1O^2) = 134.8(5)$  pm,  $\angle(O^2CO^3) = 103.2(3)^\circ$ ,  $\Theta(C^2O^2C^1O^3) = -176.7(5)^\circ$ ,  $\Theta(O^2C^1O^3C^3) = 174.8(5)^\circ$ .

**Table 7.3.** Crystal data and structure refinement results of  $[(F_3C)_3CO]_2CO$ .

empirical formula	$C_9O_3F_{18}$	$\mu$ [ $mm^{-1}$ ]	2.988
M [ $g\ mol^{-1}$ ]	498.09	$F(000)$	960
T [K]	110	min / max $\Theta$ [ $^\circ$ ]	10.726 / 148.554
crystal system	orthorhombic	dimension [mm]	0.5 x 0.5 x 0.5
wavelength [ $\text{\AA}$ ]	0.71073	colour	colourless
space group	$P2_12_12_1$	reflections collected	15006
$a$ [ $\text{\AA}$ ]	10.2736(6)	independent reflections	2908
$b$ [ $\text{\AA}$ ]	10.5964(7)	data / restraints / parameters	2908 / 0 / 272
$c$ [ $\text{\AA}$ ]	13.1388(8)	goodness-of-fit on $F^2$	1.094
$\alpha = \beta = \gamma$ [ $^\circ$ ]	90	$R_1 / wR_2$ [ $I > 2\sigma(I)$ ]	0.0393 / 0.0917
$V$ [ $\text{\AA}^3$ ]	1430.33(15)	$R_1 / wR_2$ (all data)	0.0442 / 0.0952
$Z$	4	$\Delta\rho_{\max/\min}$ [ $e\ \text{\AA}^{-3}$ ]	0.61 / -0.33
$\rho_{\text{calc}}$ [ $g\ cm^3$ ]	2.339		

## 7.4. Calculated Electron Affinities of Fluorinated Molecules

The calculations on total energies and adiabatic electron affinities of fluorinated compounds presented below were performed by Tobias Schlöder, Felix Brosi and Robin Brückner.

**Table 7.4.** Total energies and adiabatic electron affinities ( $EA_{\text{adia}}$ ) of fluorinated compounds and fragments.

compound		B3LYP/aug-cc-pVTZ		
		$E_{\text{neutral}}$ [H]	$E_{\text{anion}}$ [H]	$EA_{\text{adia}}$ [kJ mol <sup>-1</sup> ]
C <sub>1</sub>	CHF <sub>2</sub>	-238.3987780		
	CF <sub>3</sub>	-337.6916380	-337.758729	-176.15
	CF <sub>4</sub>	-437.6525830	-437.609592	112.87
C <sub>2</sub>	C <sub>2</sub> F <sub>2</sub>	-275.8469450	-275.875829	-75.83
	C <sub>2</sub> F <sub>3</sub>	-375.7081390	-375.817370	-286.79
	C <sub>2</sub> F <sub>4</sub>	-475.6900440	-475.697181	-18.74
	C <sub>2</sub> F <sub>5</sub>	-575.5664200	-575.637201	-185.84
	C <sub>2</sub> F <sub>6</sub>	-675.5196410	-675.481914	99.05
	CF <sub>3</sub> CH <sub>2</sub> F	-476.9391500	-476.925230	36.55
	CHF <sub>2</sub> CHF <sub>2</sub>	-476.9303110	-476.915665	38.45
	CHF <sub>2</sub> CFH <sub>2</sub>	-377.6409830	-377.627966	34.18
	CF <sub>3</sub> CH <sub>3</sub>	-377.6700430	-377.164883	1326.30
	HC≡CF	-176.5964560		
	HC≡CCF <sub>3</sub>	-414.5057360	-414.508680	-7.73
	C <sub>3</sub>	C <sub>3</sub> F <sub>4</sub>	-513.7648100	-513.747115
C <sub>3</sub> F <sub>6</sub>		-713.5797460	-713.598724	-49.83
C <sub>3</sub> F <sub>7</sub>		-813.1270510	-813.198855	-188.52
C <sub>3</sub> F <sub>8</sub>		-913.3850450	-913.353464	82.92
C <sub>3</sub> F <sub>7</sub> H		-814.0914190	-814.088551	7.53
CH <sub>2</sub> FCF <sub>2</sub> CF <sub>3</sub>		-714.8061170	-714.793380	33.44
CF <sub>2</sub> HCHF <sub>2</sub> CF <sub>3</sub>		-714.8077980	-714.796359	30.03
CHF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>		-814.0914190	-814.076969	37.94
H <sub>2</sub> C=CF <sub>2</sub> CF <sub>2</sub>		-415.0902100	-415.134944	-117.45
H <sub>2</sub> C=CF <sub>2</sub> CF <sub>3</sub>		-514.8177750	-514.808263	24.97
<i>trans</i> -CHF=CF <sub>2</sub> CF <sub>3</sub>		-514.8207940	-514.812882	20.77
<i>cis</i> -CHF=CF <sub>2</sub> CF <sub>3</sub>		-514.8171180	-514.810508	17.35
C <sub>4</sub>	C <sub>4</sub> F <sub>9</sub>	-1050.9011390	-1050.974880	-193.61
	C <sub>4</sub> F <sub>10</sub>	-1151.2496240	-1151.239313	27.07
	CF(CF <sub>3</sub> ) <sub>2</sub>	-813.4456500	-813.541717	-252.22
	C(CF <sub>3</sub> ) <sub>3</sub>	-1050.6947790	-1050.824165	-339.70
	(C <sub>2</sub> F <sub>5</sub> )CF <sub>2</sub> CF <sub>3</sub>	-1050.9155230	-1051.013133	-256.28

	(C <sub>2</sub> F <sub>5</sub> )CF(CF <sub>3</sub> ) <sub>2</sub>	-1389.1157550	-1389.164833	-128.85
	F <sub>2</sub> C=CF-CF=CF <sub>2</sub>	-751.3493409	-751.3721494	-59.88
C <sub>6</sub>	(CF <sub>3</sub> ) <sub>2</sub> CF=CF(CF <sub>3</sub> ) <sub>2</sub>	-1626.9739440		
	H <sub>2</sub> C=CF-(CF <sub>2</sub> ) <sub>2</sub> -CF=CH <sub>2</sub>	-830.0467720		
N	N(CF <sub>3</sub> ) <sub>3</sub>	-1068.0399890	-1068.0092220	80.78
	NCO	-168.0597540	-168.1891730	-339.79
NF <sub>x</sub>	NF <sub>3</sub>	-354.2220660		
	CF <sub>3</sub> NF <sub>2</sub>	-592.1462140	-592.2230790	-201.81
	CH <sub>2</sub> CFCF <sub>2</sub> NF <sub>2</sub>	-669.5249660	-669.5927120	-177.87
	ONF <sub>3</sub>	-429.4254460	-429.5493670	-325.35
	F <sub>2</sub> N=NF <sub>2</sub>	-508.7585010	-508.8566500	-257.69
	FN=CF <sub>2</sub>	-392.4250100	-392.4880510	-165.51
	FN≡NF	-309.1352280	-309.1550950	-52.16
NO <sub>x</sub>	NO	-129.6604754		
	FNO	-229.7108082	-229.7642005	-140.18
	N <sub>2</sub> O	-184.7268570	-184.7310220	-10.94
	CH <sub>2</sub> CFCF <sub>2</sub> NO	-545.0624820	-545.1307240	-179.17
	CF <sub>3</sub> NO	-467.6824660	-467.7571140	-195.99
	CF <sub>3</sub> CNO	-505.5830870	-505.6279720	-117.85
	CF <sub>3</sub> CF <sub>2</sub> NO	-705.2761896		
	NO <sub>2</sub>	-205.1517190	-205.2343290	-216.89
	NO <sub>2</sub> F	-305.0024300	-305.0802970	-204.44
	CF <sub>3</sub> NO <sub>2</sub>	-542.9154500	-542.9721650	-148.91
	C <sub>2</sub> F <sub>5</sub> NO <sub>2</sub>	-780.7830900	-780.8438730	-159.59
	(CF <sub>3</sub> ) <sub>2</sub> CFNO <sub>2</sub>	-1018.6541400	-1018.7171880	-165.53
	CF <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>	-582.2295530	-582.2683350	-101.82
	CF <sub>3</sub> CH <sub>2</sub> ONO <sub>2</sub>	-657.4402900	-657.5160580	-198.93
CN	FCN	-192.6210605	-192.6400638	-49.89
	(FCN) <sub>2</sub>	-385.2324632	-385.2853784	-138.93
	CF <sub>3</sub> CN	-430.6059110	-430.6103240	-11.59
	CF <sub>3</sub> OCN	-505.8462590	-505.8899860	-114.81
	(CF <sub>3</sub> ) <sub>2</sub> CFCN	-905.9948957	-906.0523723	-150.90
	(CF <sub>3</sub> ) <sub>3</sub> CCN	-1143.7870909	-1143.8151069	-73.56
	FOCN	-267.8360780	-267.9095270	-192.84
	(OCN) <sub>2</sub>	-336.1245550		
	CN(CF <sub>2</sub> ) <sub>4</sub> CN	-1136.6974052	-1136.7361409	-101.70
R <sub>2</sub> C=O	F <sub>2</sub> CO	-313.1324480	-313.1437060	-29.56
	(CF <sub>3</sub> )FCO	-551.0006920		
	(CH <sub>3</sub> ) <sub>2</sub> CO	-193.1530300	-193.1420270	28.89
	(CF <sub>2</sub> H) <sub>2</sub> CO	-590.2697320	-590.3140660	-116.40
	(CF <sub>2</sub> H)(CH <sub>2</sub> F)CO	-490.9849130	-491.0176260	-85.89

	(CF <sub>2</sub> H)(CH <sub>3</sub> )CO	-391.7168110	-391.7227230	-15.52
	(CF <sub>3</sub> )(CF <sub>2</sub> H)CO	-689.5649280	-689.6186670	-141.09
	(CF <sub>3</sub> )(CFH <sub>2</sub> )CO	-590.2807820	-590.3228920	-110.56
	(CF <sub>3</sub> )(CH <sub>3</sub> )CO	-491.0126960	-491.0278380	-39.76
	(CH <sub>2</sub> F)(CH <sub>2</sub> F)CO	-391.6978410	-391.7184840	-54.20
	(CH <sub>2</sub> F)(CH <sub>3</sub> )CO	-292.4288330	-292.4337590	-12.93
	(CF <sub>3</sub> ) <sub>2</sub> CO	-788.8592670	-788.9198150	-158.97
	(CF <sub>3</sub> )(CF <sub>3</sub> CF <sub>2</sub> )CO	-1026.7262820	-1026.7939710	-177.72
	(CF <sub>3</sub> )(C <sub>3</sub> F <sub>7</sub> )CO	-1263.8259860	-1263.8918860	-173.02
	(CF <sub>3</sub> )(C <sub>4</sub> F <sub>9</sub> )CO	-1501.5504160	-1501.6160680	-172.37
	(CF <sub>3</sub> )(CF(CF <sub>3</sub> ) <sub>2</sub> )CO	-1264.5958730	-1264.6650290	-181.57
	(CF <sub>3</sub> )(C(CF <sub>3</sub> ) <sub>3</sub> )CO	-1501.8964720	-1501.9573870	-159.93
	(CF <sub>3</sub> )(F <sub>2</sub> CCF)CO	-826.9330550		
	(CF <sub>3</sub> )(CF <sub>3</sub> OO)CO	-938.9129110	-938.9432180	-79.57
	(CF <sub>3</sub> CF <sub>2</sub> ) <sub>2</sub> CO	-1264.5923340	-1264.6625540	-184.36
	(CF <sub>3</sub> CF <sub>2</sub> )(CF(CF <sub>3</sub> ) <sub>2</sub> )CO	-1501.8898700	-1501.9576460	-177.95
	(CF <sub>3</sub> CF <sub>2</sub> )(CF <sub>2</sub> CF(CF <sub>3</sub> ) <sub>2</sub> )CO	-1501.8832790	-1501.9467270	-166.58
	(CF <sub>3</sub> CF <sub>2</sub> )(CH(CF <sub>3</sub> ) <sub>2</sub> )CO	-1402.6570800	-1402.7167520	-156.67
	(CF <sub>3</sub> CF <sub>2</sub> )[(C <sub>2</sub> F <sub>5</sub> )(CF <sub>3</sub> )CF]CO	-1501.5582220	-1501.6187790	-158.99
	(CF <sub>3</sub> CF <sub>2</sub> )[CF <sub>3</sub> C(O)CF <sub>2</sub> ]CO	-1139.6224980	-1139.7022640	-209.43
	(CF <sub>3</sub> CF <sub>2</sub> )[(CF <sub>3</sub> ) <sub>2</sub> CFC(O)CF <sub>2</sub> ]CO	-1615.1730050	-1615.2594660	-227.00
	(CF <sub>3</sub> ) <sub>2</sub> CFCO	-926.7980490	-926.8989200	-264.84
	(CF <sub>3</sub> ) <sub>2</sub> CFCF <sub>2</sub> CO	-1163.9522690	-1164.0291240	-201.78
	OCCF(CF <sub>3</sub> )(C <sub>2</sub> F <sub>5</sub> )	-1163.9568820	-1164.0571060	-263.14
	CF <sub>3</sub> O	-412.9355630	-413.1033270	-440.46
	CF <sub>3</sub> CO	-451.0539620	-451.1130960	-155.26
	C <sub>2</sub> F <sub>5</sub> CO	-688.9223120	-688.9967240	-195.37
	C <sub>3</sub> F <sub>7</sub> CO	-926.4272350	-926.5050470	-204.30
	C <sub>4</sub> F <sub>9</sub> CO	-1164.2019170		
ROR	CF <sub>3</sub> OCF <sub>3</sub>	-750.7770010	-750.8037150	-70.14
	CF <sub>3</sub> CF <sub>2</sub> OCF <sub>2</sub> CF <sub>3</sub>	-1226.5130890	-1226.4853800	72.75
	CF <sub>2</sub> =CFOOCF <sub>2</sub>	-863.6336010	-863.8389910	-539.25
	c-C <sub>3</sub> O <sub>3</sub> F <sub>6</sub>	-938.8141500	-938.7183560	251.51
	c-C <sub>4</sub> OF <sub>8</sub>	-1026.3340698	-1026.3509113	-44.22
	c-C <sub>4</sub> O <sub>2</sub> F <sub>8</sub>	-1101.3252730	-1101.2939740	82.18
ROOR	CF <sub>3</sub> OOCF <sub>3</sub>	-825.6202603	-825.7625000	-373.45
	CF <sub>3</sub> OOCF <sub>2</sub> CF <sub>3</sub>	-1063.3977257	-1063.5449887	-386.64
	CF <sub>3</sub> OOSF <sub>5</sub>	-1348.6334030		
	CF <sub>3</sub> CF <sub>2</sub> OOCF <sub>2</sub> CF <sub>3</sub>	-1301.1756477	-1301.3277721	-399.40
ROF	CF <sub>3</sub> OF	-512.7668620	-512.9058670	-364.96
	CF <sub>3</sub> CF <sub>2</sub> OF	-750.3546638		

P	PF <sub>3</sub>	-641.1369770	-641.1394080	-6.38
	PF <sub>4</sub>	-740.9851910	-741.1052820	-315.30
	PF <sub>4</sub> (CF <sub>3</sub> )	-1078.7727610	-1078.8332370	-158.78
	PF <sub>4</sub> (CF=CF <sub>2</sub> )	-1116.8446670	-1116.8905560	-120.48
	PF <sub>5</sub>	-840.9408890	-840.9919610	-134.09
	OPF	-516.5663270		
	OPF <sub>2</sub>	-616.4455470	-616.5708700	-329.04
	OPF <sub>3</sub>	-716.4173210	-716.4400860	-59.77
	OPF <sub>2</sub> (CF <sub>3</sub> )	-954.2473110	-954.2802150	-86.39
	OP(CF <sub>3</sub> ) <sub>3</sub>	-1429.8977050	-1429.9544250	-148.92
	OP(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub>	-1773.6685380	-1773.6886460	-52.79
	OPF <sub>2</sub> (OCH <sub>2</sub> CF <sub>3</sub> )	-1068.8358760	-1068.8574470	-56.63
	OPF <sub>2</sub> (OCF=CF <sub>2</sub> )	-992.3171360	-992.3584140	-108.38
	S	SF <sub>2</sub>	-597.9381760	-598.0065770
SF <sub>5</sub> Br		-1314.4499990	-1314.5837690	-351.21
SF <sub>5</sub> C <sub>2</sub> F <sub>5</sub>		-1473.1489810	-1473.2496940	-264.42
SF <sub>5</sub> CF <sub>3</sub>		-1235.2836180	-1235.3735830	-236.20
SF <sub>5</sub> CN		-990.3673080	-990.4666830	-260.91
SF <sub>5</sub> NF <sub>2</sub>		-1151.9109980	-1152.0501010	-365.21
SF <sub>5</sub> OCF <sub>3</sub>		-1310.5367290	-1310.6547210	-309.79
SO <sub>2</sub> (CF <sub>3</sub> ) <sub>2</sub>		-1224.1612440	-1224.2313800	-184.14
SOF <sub>2</sub>		-673.2207830	-673.2825700	-162.22
SO <sub>2</sub> F <sub>2</sub>		-748.4459280	-748.5175480	-188.04
SO <sub>2</sub> FBr		-1065.4852530	-1065.6012700	-304.60
SO <sub>2</sub> FC <sub>2</sub> F <sub>3</sub>		-1024.3729390	-1024.4291630	-147.62
SO <sub>2</sub> FOCF <sub>3</sub>		-1061.5693380	-1061.6724660	-270.76
SO <sub>2</sub> FOCH <sub>2</sub> CF <sub>3</sub>		-1100.8710710	-1100.9430510	-188.98
SO <sub>2</sub> (OCH <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>		-1453.2956980	-1453.3631300	-177.04
S(O)(CF <sub>3</sub> ) <sub>2</sub>		-1148.9287460	-1148.9808960	-136.92
S(O)F <sub>4</sub>		-872.9015330	-873.0159160	-300.31
<i>trans</i> -SF <sub>4</sub> Br <sub>2</sub>		-1631.4805080	-1631.6193630	-364.56
<i>trans</i> -SF <sub>4</sub> (CF <sub>3</sub> ) <sub>2</sub>		-1473.1490720	-1473.2407510	-240.70
<i>trans</i> -SF <sub>4</sub> (OCF <sub>3</sub> ) <sub>2</sub>		-1623.6532680	-1623.7766720	-324.00
S(CF <sub>3</sub> ) <sub>2</sub>		-1073.7300090	-1073.7354060	-14.17
SF <sub>2</sub> (CF <sub>3</sub> ) <sub>2</sub>		-1273.4329620	-1273.4825780	-130.27
SF <sub>4</sub> (CF <sub>3</sub> ) <sub>2</sub>		-1473.1341060	-1473.2191700	-223.34
SF <sub>5</sub> CF <sub>2</sub> CF <sub>3</sub>		-1273.3429290	-1273.4245020	-214.17
SF <sub>5</sub> CFO		-1110.7703320	-1110.8574090	-228.62
SF <sub>5</sub> CO		-1010.8692480		
SF <sub>5</sub> C(O)C(CF <sub>3</sub> ) <sub>3</sub>		-1348.6334030		
SF <sub>3</sub> C <sub>2</sub> F <sub>3</sub>		-1073.4077080		

	SF <sub>3</sub> CF <sub>2</sub> CF <sub>3</sub>	-1273.1560460		
	SF <sub>5</sub> CCH	-974.2673650	-974.3429940	-198.56
	SF <sub>5</sub> NCO	-1065.6576800	-1065.7615450	-272.70
	SF <sub>5</sub> OCN	-1065.6097010	-1065.7523880	-374.62
	SF <sub>5</sub> NO	-1027.2741780	-1027.4226060	-389.70
	CF <sub>3</sub> CF <sub>2</sub> SF	-1073.4929470	-1073.5745260	-214.19
	NSF <sub>2</sub>	-652.6384580	-652.7793270	-369.85
	N <sub>2</sub> S <sub>2</sub> F <sub>4</sub>	-1305.1540120		
	CFCF <sub>2</sub> NSF <sub>2</sub>	-1067.6244230	-1067.7020730	-203.87
	SNF <sub>3</sub>	-752.5090210	-752.6044200	-250.47
	CF <sub>3</sub> NSF <sub>2</sub>	-990.4677560	-990.5512310	-219.16
	c-SF <sub>4</sub> C <sub>2</sub> F <sub>4</sub>	-1273.3193640	-1273.4422810	-322.72
	SF <sub>4</sub> CC(CF <sub>3</sub> ) <sub>2</sub>	-1511.2260040	-1511.3452870	-313.18
	CF <sub>3</sub> S(O) <sub>2</sub> OCF <sub>3</sub>	-1299.4296030	-1299.5342760	-274.82
	SF <sub>3</sub> CF <sub>3</sub>	-1035.3533530	-1035.4466140	-244.86
	SF <sub>3</sub> C <sub>2</sub> F <sub>5</sub>	-1273.4240970	-1273.5056540	-214.13
other	ClO <sub>3</sub> F	-785.5248390	-785.6519530	-333.74
	SeF <sub>6</sub>	-972.4485870	-972.5951430	-384.78
	(CF <sub>3</sub> )SiMe <sub>3</sub>	-746.2418440	-746.2309820	28.52
	BF <sub>3</sub>	-324.6888300	-324.6746740	37.17
	B <sub>2</sub> F <sub>4</sub>	-449.4749200	-449.5043890	-77.37
	SiF <sub>4</sub>	-689.3205260	-689.3045660	41.90



