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From Hypochlorites to Perfluorinated Dialkyl Peroxides

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Graphical abstract



A new member of the hypochlorite family, undecafluoro-*tert*-pentyl hypochlorite, $(C_2F_5)(F_3C)_2COCI$, is presented. Hypochlorites, R^FOCI, are ideal precursors for the assembly line production of perfluorinated dialkyl peroxides, R^FOOR^F. After short irradiation at lower temperatures, the product can be "barrelled".

Highlights

- convenient syntheses of reactive perfluoro alkylhypochlorites, RFOCI, are reported
- the novel undecafluoro-tert-pentyl hypochlorite, (C2F5)(F3C)2COCI is reported for the first time
- the hypofluorites were characterized by gas-phase IR, UV/Vis and NMR spectroscopy
- quantum-chemical calculations at the DFT and MP2 levels are provided
- the use of hypochlorites for a suitable route to otherwise difficult to access perfluorinated dialkyl peroxides, R^FOOR^F is reported

Abstract: The synthesis and characterization of the new perfluorinated hypochlorite, undecafluoro-*tert*-pentyl hypochlorite, $(C_2F_5)(F_3C)_2COCI$, is reported. Its gas-phase infrared, UV/Vis and NMR spectra have been recorded and its spectroscopic properties are discussed and compared with quantum-chemical predictions and those of other known perfluorinated hypochlorites such as R^FOCI [R^F = F₃C, (F₃C)₃C, (C₂F₅)(F₃C)₂C]. A synthetic route to otherwise difficult to access perfluorinated dialkyl peroxides, R^FOOR^F, is also provided by low-temperature photolysis of the corresponding hypochlorite.

Keywords: hypochlorites • radical reactions • photochemistry • perfluoro dialkyl peroxides

1. Introduction

Perfluorinated hypochlorites such as F_3COCI and F_5SOCI were first introduced by Anderson and co-workers in 1968,[1] twenty years after the related trifluoromethyl hypofluorite, F_3COF , was synthesized by Cady and co-workers.[2] Although these hypohalites are closely related to each other, their reactivities show significant differences. While the hypofluorite F_3COF reacts with olefins (e.g. $H_2C=CCI_2$ or $H_2C=CF_2$) in a free radical mechanism with poor or no stereoselectivity and regioselectivity forming anti-Markovnikov products [Equation (1a)], the hypochlorite F_3COCI exclusively results in

Markovnikov products by *syn*-addition with a high stereoselectivity [Equation (1b)].[3] Hypochlorite compounds, ROCI, are valuable precursors for chloroformiates, ROC(O)CI,[4,5] and chlorosulfates, ROSO₂CI, which are formed by insertion of

$H_2C=CX_2$	$\xrightarrow{F_3COF}$	F ₃ CO-CH ₂ -CX ₂ -F	anti-Markovnikov	(1a)
$H_2C=CX_2$	$\xrightarrow{F_3COCl}$	F ₃ CO-CX ₂ -CH ₂ -Cl	Markovnikov	(1b)
with $X = 0$	CI. F			

CO or SO₂, respectively, into the O–Cl bond.[6] The experimental O–X bond dissociation energy (BDE) of F₃COCI[7], 221±8 kJ mol⁻¹, is slightly higher than that for F₃COF[8] (BDE = 184.2 kJ mol⁻¹), but is still relatively low. Besides the addition of hypochlorites to the double bonds of (halo)olefins to form ethers,[3,9] they also react with several sulfanes[10,11] and phosphorus[12] compounds, e.g. (F₃C)₂S or PCl₃. Nonafluoro-*tert*-butyl hypochlorite, (F₃C)₃COCl, undergoes oxidative displacement or addition reactions with metal chlorides, e.g. VOCl₃ [Equation (2a)] or TiCl₄ [Equation (2b)], and elements such as bismuth [Equation (2c)] or tellurium [Equation (2d)].[13] F₃COCl can be synthesized batchwise[1] or in a continuous process[14]. Upon photolysis, it forms trifluoromethoxy radicals, F₃CO⁻, which recombine to provide the symmetrically substituted bis(trifluoromethyl) peroxide, (F₃CO)₂.[9] The bulkier bis(nonafluoro-*tert*-butyl alcohol, (F₃C)₃COF, with the strong oxidizer chlorine trifluoride, CIF₃,[15] ii) treatment of nonafluoro-*tert*-butyl hypofluorite, (F₃C)₃COF with partially fluorinated silver wool[17].

VOCI ₃	$\xrightarrow{+3 (F_3C)_3 \text{COCl}}$	3 Cl ₂ + [VO(OC(CF ₃) ₃) ₃]	(2a)	
TiCl ₄	$\xrightarrow{+ 4 (F_3C)_3 \text{COCl}}$	4 Cl ₂ + [Ti(OC(CF ₃) ₃) ₄]	(2b)	
2 Bi	$\xrightarrow{+ 6 (F_3C)_3 \text{COCl}}$	3 Cl ₂ + 2 [Bi(OC(CF ₃) ₃) ₃]	(2c)	
Те	$\xrightarrow{+ 4 (F_3C)_3 \text{COCl}}$	2 Cl ₂ + [Te(OC(CF ₃) ₃) ₄]	(2d)	

A general route to hypochlorites is the addition of chlorine monofluoride, CIF, to a carbonyl compound [Equation (3a)] or the reaction of CIF with alcohols by elimination of hydrogen fluoride, see Equation (3b). The HF by-product is trapped during the reaction by an excess of CsF, which reacts further to form CsHF₂.[18] CIF was synthesized as reported previously either in a flow process by addition of chlorine gas, Cl₂, to a constant stream of fluorine gas, F₂, at 400 °C, or batchwise from stoichiometric amounts of chlorine trifluoride, CIF₃, and Cl₂ at 180 °C.[19] The reaction of dichlorine monoxide, Cl₂O, with carbonyl fluoride, F₂CO, was also shown to yield F₃COCI in the presence of CsF.[20]

RR'C=O + CIF	$\xrightarrow{\text{CsF}}$	RR'FC-OCI	(3a)
RR'R''C-OH + CIF	$\xrightarrow{\text{CsF}}$	RR'R"C-OCI + CsHF ₂	(3b)
with R, R', R" =	F, CF ₃ , C ₂ F ₅		

2. Results and Discussion

2.1. Perfluorinated Hypochlorites

The perfluoroalkyl trifluoromethyl hypochlorite, F_3COCI (**1a**), was obtained according to Equation (2a) by treatment of F_2CO with CIF in a stainless steel reactor in the presence of CsF,[20] while the bulkier nonafluoro-*tert*-butyl hypochlorite, $(F_3C)_3COCI$ (**1b**)[6] and undecafluoro-*tert*-pentyl hypochlorite, $(C_2F_5)(F_3C)_2COCI$ (**1c**) were formed by the reaction of the corresponding alcohol $(F_3C)_3COH$ and $(C_2F_5)(F_3C)_2COH$, respectively, with CIF in the presence of CsF [Equation (2b)]. The mixtures were initially cooled to -196 °C, and then slowly warmed to room temperature while shaking the stainless steel vessel. The gas-phase IR spectra of the perfluorinated hypohalites are in good agreement with the previously reported spectra (see Figure S2.3 in the Supporting Information).[1,6] The O–Cl stretching modes of these hypochlorites are observed in a narrow range between 780 cm⁻¹ and 790 cm⁻¹ (see Table 1), where the O–Cl stretching mode of **1b** at 785 cm⁻¹ couples with the nearby symmetric CF₃ deformation modes at 755, 733 and 730 cm⁻¹.

Table 1. Frequencies of the ν (O–CI) stretching modes (in cm⁻¹) and maxima of the strongest electronic transitions in the UV/Vis spectra (in nm) of selected hypochlorites R^FOCI.

R^F ν(O-Cl) [cm⁻¹] λ_{max} [nm]

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				-		
	exp.	DFT ^[a]	ref.	exp.	DFT ^[b]	ref.
F ₃ C (1a)	787	775	789[9]	239	248.5	/
(F ₃ C) ₃ C (1b)	785	782	788[6]	255	260.6	256 ^[c]
(C ₂ F ₅)(F ₃ C) ₂ C (1c)	781	773	/	255	/	/

[a] B3LYP/aug-cc-pVTZ.

[b] TD-B3LYP/def2-TZVPP.

[c] In FC-75 solution, see reference [13].

The gas-phase IR spectrum of $(C_2F_5)(F_3C)_2COCI$ (**1c**) is shown in Figure 1. It consists of strong absorption bands from about 1300 to 1200 cm⁻¹ assigned to C–F stretching modes, whereas the symmetric CF₃ deformation bands appear at 743 and 728 cm⁻¹ (Table 2). The bands in the mid-IR region from 1102 to 888 cm⁻¹ split into two components most likely due to the presence of at least two rotational conformers of **1c** in the gas phase. This assumption is supported by quantum-chemical calculations at the B3LYP level, which predict two conformers **1c**, of which the *gauche* structure is energetically favored by about 10 kJ mol⁻¹ (see Figure 2 and Supporting Information Figure S3.1). As previously shown for the corresponding undecafluoro-*tert*-pentyl hypofluorite, $(C_2F_5)(F_3C)_2COF$ [17], the different conformers display slightly different IR spectra (Table 2). The hypochlorite bands of **1c** at 1102 and 1083 cm⁻¹ are tentatively assigned to C–O stretching modes of the *trans* and *gauche* conformer, (Table 2), while bands in the region from 998 to 888 cm⁻¹ are assigned to C–C vibrations. For the O–CI stretching mode of **1c**, the calculations predict very weak bands at 768 for the *trans*- and at 773 cm⁻¹ for the *gauche*-conformer, respectively. As previously described for (F₃C)₃COCI (**1b**), the O–CI stretching mode of **1c** is strongly coupled with the symmetric CF₃ deformation modes located at 755, 743 and 728 cm⁻¹. The weak band at 630 cm⁻¹ is assigned to the CC₃ deformation, while the asymmetric CF₃ deformation modes are observed at 542 and 530 cm⁻¹. These assignments are consistent with the calculated band positions for *gauche*-**1c** at 631, 537 and 525 cm⁻¹.



Figure 1. Gas-phase IR spectrum of $(C_2F_5)(F_3C)_2COCI$ (**1c**) (bottom trace, 10 cm IR cell) compared with the computed spectrum of the *gauche* conformer at the DFT B3LYP/aug-cc-pVTZ level of theory (top trace, for the *gauche* conformer of **1c**, see Figure 2).



Figure 2. Relative energies ΔE° for the rotational *trans* and *gauche* conformers of (C₂F₅)(F₃C)₂COCI (**1c**) calculated at the DFT B3LYP/aug-cc-pVTZ level of theory. Fluorine atoms are omitted for clarity (see Figure S3.1 in the Supporting Information).

Table 2. Gas-phase IR vibrational frequencies $\tilde{\nu}$ [cm⁻¹] and relative IR band intensities^[a] compared with the computed values of the *trans* and *gauche* rotational conformers^[b] of (C₂F₅)(F₃C)₂COCI (**1c**) at B3LYP/augcc-pVTZ level.

exp.	D	DFT		
	trans	trans gauche		
1342 (m)	1287 (96)	1309 (26)	$v(F_3C-CF_2)$	
1282 (s, sh)	1266 (239)	1252 (385)	v(CF ₃)	
1270 (vs)	1248 (588)	1244 (507)	$v(CF_3)$	
1252 (vs)	1237 (357)	1234 (357)	v(CF ₃)	
1228 (s)	1231 (61)	1222 (232)	v(CF ₃)	
	1215 (149)	1218 (198)	v(CF ₃)	

1204 (m, sh)	1195 (282)	1198 (251)	ν(CF ₃)
	1181 (49)	1187 (2)	v(CF ₃)
	1161 (30)	1154 (1)	v(CF ₃)
1173 (m)	1151 (49)	1149 (16)	v(CF ₃)
1148 (mw)	1120 (6)	1126 (16)	$v(CF_2)$
1102 (m), 1083 (mw)	1063 (109)	1101 (39)	v(CO)
1041 (vw)	1041 (40)	1062 (69)	$v(C-CF_2)$
998 (m), 987 (m), 974 (m)	969 (102)	960 (95)	$v(C-(CF_3)_2)$
901 (m, sh), 888 (m)	936 (153)	900 (142)	$v(C-(CF_3)_2)$
781 (vw)	768 (5)	773 (1)	v(OCI)
755 (w, sh)	752 (15)	751 (4)	δ(CF ₃)
743 (m)	729 (37)	739 (57)	δ(CF ₃)
728 (ms)	720 (36)	722 (38)	δ(CF ₃)
630 (w)	638 (8)	631 (7)	δ(CF ₂)
542 (w)	537 (3)	537 (3)	δ(CF ₃)
530 (w)	523 (9)	525 (9)	δ(CF ₃)
n.o.	488 (4)	489 (5)	δ(CF ₃)
n.o.	444 (2)	442 (2)	δ(C ₂ F ₅)

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very

weak, sh = shoulder, n.o. = not observed.

[b] See Figure 2.

The ¹⁹F NMR spectrum of hypochlorite **1c** is shown in Figure 3. The septet at $\delta = -116.9$ ppm, assigned to the CF₂ moiety, exhibits a large ⁴J coupling constant of 12 Hz to the fluorine nuclei of the two CF₃ groups bound to C_a. A septet with a ⁵J coupling constant of 6 Hz appeared at $\delta = -81.6$ ppm for the fluorine atoms of the terminal CF₃ group, and the signal for the two equivalent CF₃ groups is observed at $\delta = -69.1$ ppm as a triplet of quartets. The ³J coupling constant between the fluorine atoms of the pentafluoro ethyl group is < 0.5 Hz. Similar chemical shifts and coupling constants were observed for undecafluoro-*tert*-pentyl hypofluorite, (C₂F₅)(F₃C)₂COF.[17] In the fully coupled ¹³C NMR spectrum of **1c** (see Figure S2.4 in the Supporting Information), the resonance of the quaternary carbon atom at $\delta = 84.0$ ppm is split into a septet of triplets with ²J(FC) coupling constants of 31 Hz with the fluorine atoms of the CF₃ groups at C_a show a quartet at $\delta = 119.4$ ppm [¹J(FC) = 293 Hz], but the quartet of the terminal CF₃ group bonded to the bridging C atom is at $\delta = 117.2$ ppm and is further split into triplets due to a ²J(FC) coupling of 34 Hz with the fluorine atom at $\delta = 110.8$ ppm is split into a triplet of quartets.



Figure 3. ¹⁹F NMR spectrum of (C₂F₅)(F₃C)₂COCI (1c) (376.88 MHz, neat, external [D₆]Acetone, 20.5 °C).

The gas-phase UV/Vis spectra of the hypochlorites **1a,b,c** show strong transitions at 239 nm for **1a** and 255 nm for **1b** [13] and **1c** (Figure 4). According to TD-DFT calculations (Table 1 and Tables S3.2 and S3.3 in the Supporting Information), these major absorptions are mainly due to HOMO–1 [$(n_{Cl}-n_{O})_{i.p.}$] \rightarrow LUMO [$\sigma^*(OCl)$] transitions, that originate from the inplane, non-bonding combination, [$(n_{Cl}-n_{O})_{i.p.}$], and are predicted at 248.5 nm for **1a** and at 260.6 nm for **1b**. The much weaker HOMO [$(n_{Cl}-n_{O})_{o.o.p.}$] \rightarrow LUMO [$\sigma^*(OCl)$] transitions, originating from the out-of-plane non-bonding combination, [$(n_{Cl}-n_{O})_{o.o.p.}$], are predicted at 299.5 nm for **1a** and 323.0 nm for **1b** (Table S3.2 in the Supporting Information). Although the bulky hypochlorites **1b** and **1c** exhibit weak shoulders at about 330 nm in the UV/Vis spectrum, this lowest-energy transition appeared in the gas-phase UV/Vis spectrum of trifluoromethyl hypochlorite F₃COCl (**1a**) between 300 to 450 nm as a weak band with pronounced vibrational fine structure corresponding to the O–Cl stretching mode in the electronically excited state (Figure S2.5, left, and Table S2.1 in the Supporting Information). The origin of this transition occurs at 461 nm and the vibrational spacing of this progression has been analyzed by a linear Birge-Sponer plot[21,22], resulting in a fundamental frequency of 706±12 cm⁻¹ (Figure S2.6 left, in the Supporting Information), which represents the v(O–Cl) fundamental stretching frequency in the electronically excited state. The progression revealed a maximum intensity at v' = 11 (λ = 344 nm). This excited state v(O–Cl) stretching frequency is bathochromically shifted by approximately 75 cm⁻

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¹ relative to the fundamental in the ground electronic state of **1a** (781 cm⁻¹, Table 2). Assuming a simple two-mass dependent Morse potential for the O–Cl bond stretching mode, the linear Birge-Sponer extrapolation procedure[21,22] may also provide a rough estimate of the excited state O–Cl bond dissociation energy of $D_0 = 12682 \text{ cm}^{-1}$ (152 kJ mol⁻¹) for **1a**, which is approximately 70 kJ mol⁻¹ lower in energy than experimental value in the ground electronic state.[7]

Although no vibrational fine structure is observed in the UV/Vis spectrum of $(F_3C)_3$ COCI (**1b**), such fine structure is barely apparent in the weak shoulder at about 330 nm for $(C_2F_5)(F_3C)_2$ COCI (**1c**, Figure S2.5 and Table S2.1 in the Supporting Information). Analysis of this fine structure yielded a band that originates at 433 nm, whereas the vibrational band with highest intensity corresponds to v' = 7 (λ = 359 nm). The v(O–CI) stretching mode in the electronically excited state is redshifted by about 83 cm⁻¹ [v'(O–CI) = 705±21 cm⁻¹, Figure S2.6 right, in the Supporting Information] compared to the O–CI stretching frequency of **1c** in electronic ground state at 781 cm⁻¹. The O–CI bond dissociation energy extrapolated by the Birge-Sponer procedure[21,22] for **1c** in the excited state, with D_0 = 12346 cm⁻¹ (148 kJ mol⁻¹), is slightly smaller than that of **1a**.

The BDEs for a homolytic cleavage of the O–X bond in the hypohalites, $R^{F}OX$ ($R^{F} = F_{3}C$, $(F_{3}C)_{3}C$, $(C_{2}F_{5})F_{3}C)_{2}C$; X = F, Cl), were calculated at the B3LYP/aug-cc-pVTZ level of theory (Table S3.4 and Table S3.5 in the Supporting information). The calculated BDE for the hypochlorite, $F_{3}COCI$, of 198 kJ mol⁻¹ is slightly underestimated compared to the experimental value of 221±8 kJ mol⁻¹[7], but the calculated BDE of the hypofluorite, $F_{3}COF$, of 180 kJ mol⁻¹ is in good agreement with the experiment (184.2 kJ mol⁻¹)[8]. The tertiary hypohalites ($F_{3}C)_{3}COX$ and ($C_{2}F_{5})(F_{3}C)_{2}COX$ display similar BDEs for O–Cl and the O–F bond cleavages of 150 to 160 kJ mol⁻¹, whereas the O–Cl bond is about 5 kJ mol⁻¹ more stable than O–F.



Figure 4. UV/Vis spectra of the perfluorinated hypochlorites F_3COCI (1a, solid line), $(F_3C)_3COCI$ (1b, dashed line) and $(C_2F_5)(F_3C)_2COCI$ (1c, dotted line) in the gas phase shown from 200 to 600 nm (10 cm UV/Vis cell, 50 mbar).

2.2. Perfluorinated Peroxides

According to the procedure described previously[9], the peroxide (F₃CO)₂ (2a) was produced in a yield of 91% by photolysis of F₃COCI (1a) using a Xenon high-pressure arc lamp at room temperature, together with a stoichiometric amount of Cl₂ and traces of F_2CO and SiF_4 . In an attempt to also synthesize the peroxides ($C_2F_5O_2$ (2d) and [($F_3C_2FCO_2$ (2e), the hypochlorites C₂F₅OCI (1d) and (F₃C)₂FCOCI (1e) were initially synthesized according to Anderson and co-workers [Equation (3a)][20] and then irradiated at -78 °C for 1 h in a guartz vessel. However, after the reaction products were separated by trap-to-trap distillation, the respective sole decomposition products (1d: F₃CCl and F₂CO, 1e: F₃CCl and $F_3CC(O)F$) were identified by their gas-phase IR spectra. [23–25]. It is assumed that the alkoxy radicals R^FO^{*}, initially formed under these reaction conditions, are rather unstable and decompose by C-C cleavage [Equation (4a)] rather than by combination to form a peroxide bond [Equation (4b)]. This assumption is supported by a recent computational study in which the activation energy for C–C bond cleavage of the C_2F_5O radical was computed at 14.0 and 34.2 kJ mol⁻¹ at the B3LYP/cc-pVTZ or G3(MP2) levels of theory, respectively[26]. Irradiation of trifluoroethyl hypochlorite, F₃CCH₂OCI (1f), led to different decomposition behavior. After irradiation for 1 h at -78 °C, the main product identified by IR-spectroscopy was trifluoroacetaldehyde, F₃CC(O)H [27]. Obviously, cleavage of a C-H bond in the intermediate alkoxy radical is preferred over C–C bond cleavage or radical dimerization to the desired bis(trifluoroethyl) peroxide (F₃CCH₂O)₂. The course of this reaction is consistent with a recent report in which the activation energy for the C-C bond cleavage in the F₃CCH₂O[•] radical was calculated to be three times higher (B3LYP/cc-pVTZ: 89.9 kJ mol⁻¹; G3(MP2): 101.7 kJ mol⁻¹)[26] than that for the perfluorinated $C_2F_5O^{\bullet}$ radical.

$$F_{3}CRFC-OCI \xrightarrow{h\nu} CI' + F_{3}CRFC-O' \xrightarrow{-F_{3}C'} RFC=O$$
(4a)
$$\xrightarrow{x \ 2} F_{3}CFRC-OO-CRFCF_{3}$$
(4b)

with $R = F \mathbf{1d}$ $CF_3 \mathbf{1e}$

The photolysis of $(F_3C)_3$ COCI (**1b**) at room temperature for 1 h also failed to yield the desired bis(nonafluoro-*tert*-butyl) peroxide (**2b**). Only F_3CCI and $(F_3C)_2CO$ were identified as reaction products by IR spectroscopy[23,27]. However, when the irradiation was carried out at 0 °C, the symmetrical peroxide [(F_3C)_3CO]₂ (**2b**) was obtained in 10 to 20 % yields and identified by its gas-phase IR and NMR spectra[17] [Equation (5)]. The yield further increased up to 80 % when the reaction mixture was cooled to -78 °C during photolysis. As shown in Figure 5, the decomposition of hypochlorite **1b** to F_3CCI and (F_3C)₂CO is thermodynamically preferred [reaction energies of **1b** are -168.9 kJ mol⁻¹ (B3LYP/aug-cc-pVTZ) and -188.4 kJ mol⁻¹ (MP2/aug-cc-pVTZ)] compared to the kinetically favored formation of peroxide **2b** (B3LYP/aug-cc-pVTZ: -6.6 kJ mol⁻¹; MP2/aug-cc-pVTZ: -6.7 kJ mol⁻¹). By analogy, irradiation of (C_2F_5)(F_3C)₂COCI (**1c**) at room temperature resulted in decomposition to C_2F_5CI and (F_3C)₂CO, as shown by their gas-phase IR and NMR spectroscopy.[17] Note that the purification of the peroxide **2** can be complicated by the presence of traces of alcohols, because the hypochlorites **1b** and **1c** are very sensitive to moisture and react instantaneously with traces of water to form their corresponding alcohols. These alcohols are hard to remove from peroxide **2** by distillation. The mixture can be purified by adding the photolysis products to CsF, from which the peroxide **2** can be removed easily.

(5)		$1/2 Cl_2 + (F_3C)_2RC-OO-CR(CF_3)_2$	$\xrightarrow{h\nu, T}$	(F ₃ C) ₂ RC–OCI
	80%	with $R = CF_3 2b$		with $R = CF_3 \mathbf{1b}$
	50%	C ₂ F ₅ 2c		C ₂ F ₅ 1c

Photolysis of a 1:1 mixture of F_3COCI (1a) and $(F_3C)_3COCI$ (1b) at 0 and -78 °C yields the symmetric dialkyl peroxides $(F_3CO)_2$ (2a) and $[(F_3C)_3CO]_2$ (2b) instead of the asymmetric dialkyl peroxide $F_3COOC(CF_3)_3$. Considering the reactants' vapor pressures under the given reaction conditions (Figure S2.7 in the Supporting Information), 1a is gaseous and 1b is a liquid. Thus, peroxide 2a is most likely formed in the gas phase, but 2b forms separately in the liquid phase.



Figure 5. Calculated reaction energies [in kJ mol⁻¹] for the photolysis products of (F₃C)₃COCl (**1b**) to yield either chlorine and bis(nonafluoro-*tert*butyl) peroxide (**2b**, left) or F₃CCl and (F₃C)₂CO via CF₃ radical elimination from the initially formed nonafluoro *tert*-butoxy radical (right) at the B3LYP/aug-cc-pVTZ (**bold**) and MP2/aug-cc-pVTZ (*italic*) levels of theory (for structures and atomic coordinates, see Figure S3.2 and Table S3.6, respectively, in the Supporting Information).

3. Conclusions

A convenient synthesis for the reactive perfluoro alkylhypochlorites, $R^{F}OCI$, is reported and the family of the known $R^{F}OCI$ compounds is expanded by the novel synthesis and structural characterization of the undecafluoro-*tert*-pentyl hypochlorite, $(C_2F_5)(F_3C)_2COCI$. The hypofluorites were characterized by their gas-phase IR-, UV/Vis and NMR spectra, and their spectroscopic properties are discussed based on quantum-chemical calculations at the DFT and MP2 levels, and are compared with the related hypofluorite compounds, $R^{F}OF$. The hypochlorites can be easily handled in glass vessels and their photolyses are shown to provide particularly suitable routes to otherwise difficult to access perfluorinated dialkyl peroxides, $R^{F}OOR^{F}$.

4. Experimental

Safety Note: Extreme caution should be exercised when handling the strongly oxidizing compounds chlorine, chlorine monofluoride, chlorine trifluoride, carbonyl fluoride and hypochlorites because of their very high reactivities and hazardous properties. We recommend wearing suitable protective equipment such as leather gloves, face shields and ear protection. Although the described perfluoroalkyl peroxides were found to be insensitive to shock and friction[29] according to the UN Recommendations on the Transport of Dangerous Goods[30], we cannot exclude explosive reactions in mixtures of these perfluoroalkyl peroxides with other substances.

(F₃C)₃COCI: The preparation of nonafluoro-*tert*-butyl hypochlorite is described elsewhere.[6] IR (gas): \tilde{v} [cm⁻¹] = 1346 (w, sh), 1322 (m, sh), 1300 (s), 1287 (vs), 1269 (s), 1264 (s), 1218 (w), 1192 (w), 1103 (m), 1004 (m), 981 (m), 785 (vw), 755 (w), 733 (m), 730 (m), 549 (w), 543 (w), 539 (w), 491 (w). UV/Vis (gas): λ [nm] = 255, 330.

(C_2F_5)(F_3C)₂COCI: Freshly distilled undecafluoro-*tert*-pentyl alcohol (1.816 g, 6.35 mmol) was added to CsF (50 g) in a stainless steel reactor (V =720 mL) by condensation at liquid nitrogen temperature. The reactor was rapidly warmed to room temperature and vigorously shaken. After cooling to -196 °C again, CIF was added (4.0 bar, 54.2 ml, 8.75 mmol, 1.38 eq.). The liquid nitrogen was removed and the empty cold dewar replaced around the steel reactor. While slowly warming to r.t. the reactor was shaken occasionally. The crude product was collected in an external cold trap and a subsequent trap-to-trap distillation (-65 °C / -90 °C / -196 °C) led to pure undecafluoro-*tert*-pentyl hypochlorite at -90 °C as a colorless solid (1.9 g, 6 mmol, 95 %), besides C₂F₅Cl and (F₃C)₂C(O) at -196 °C. ¹³C NMR (neat, external [D₆]acetone, 21.6 °C): δ [ppm] = 119.4 (q, ¹J_{FC} = 293 Hz, C(CF₃)₂), 117.2 (qt, ¹J_{FC} = 287 Hz, ²J_{FC} = 34 Hz, CF₃), 110.8 (tq, ¹J_{FC} = 275 Hz, ²J_{FC} = 41 Hz, CF₂), 84.0 (tsept, ²J_{FC} = 31, 26 Hz, C_q). ¹⁹F NMR (neat, external [D₆]acetone, 20.5 °C): δ [ppm] = -69.1 (tq, 6F, ⁴J = 12 Hz, ⁵J_{FF} = 6 Hz, C(CF₃)₂), -81.6 (sept, 3F, ⁵J_{FF} = 6 Hz, CF₃), -116.9 (sept, 2F, ⁴J_{FF} = 12 Hz, ⁵J_{FF} = 6 Hz, CF₂). IR (gas): \hat{v} [cm⁻¹] = 1342 (m), 1282 (vs, sh), 1270 (vs), 1252 (vs), 1228 (s), 1172 (w), 1101 (m), 1083 (m), 998 (m), 987 (m), 973 (m), 928 (w), 905 (m, sh), 895 (m, sh), 888 (m), 781 (vw), 755 (w, sh), 743 (m), 728 (ms), 630 (w), 542 (w), 530 (w). UV/Vis (gas): λ [nm] = 255, 359.

[(F₃C)₃CO]₂: Nonafluoro-tert-butyl hypochlorite (4.0 mmol) was transferred by condensation at liquid nitrogen temperature into a guartz vessel. The vessel was then cooled with dry ice and irradiated for 1 h. The reaction mixture was collected in an external cold trap. Subsequent trap-to-trap distillation (-45 °C / -78 °C / -196 °C) led to pure bis(nonafluoro-tert-butyl) peroxide at -78 °C as a colorless solid (1.6 mmol, 80 %). The NMR and IR spectra match with those previously reported.[15,17] ¹³C{¹⁹F} DEPTQ NMR (neat, external [D₆]acetone, r.t.): δ [ppm] = 118.8 (CF₃), 84.3 (C_q). ¹⁷O NMR (54.19 MHz, neat, external [D₆]acetone, r.t.): δ [ppm] = 246 (s). ¹⁹F NMR (neat, external [D₆]acetone, r.t.): δ [ppm] = -69.6 (s). IR (gas): \tilde{v} [cm⁻¹] = 1311 (s, sh), 1302 (s, sh), 1288 (vs), 1259 (s), 1226 (w), 1110 (s), 1002 (m), 982 (m), 772 (vw), 739 (m), 731 (m), 541 (w), 496 (w). Raman (solid): \tilde{v} [cm⁻¹] = 1311 (m, sh), 1294 (m), 1278 (m, sh), 1129 (s), 1027 (s), 872 (m, sh), 865 (s), 783 (vs), 771 (w), 749 (s), 691 (vw), 569 (w), 545 (m, sh), 541 (m), 523 (w), 356 (m), 339 (m), 326 (s, sh), 319 (s), 305 (m), 296 (w), 266 (w), 260 (w, sh), 241 (s), 194 (w), 123 (s), 118 (m, sh). UV/Vis (gas): λ [nm] = 253. [(C2F5)(F3C)2CO]2: Undecafluoro-tert-pentyl hypochlorite (4.0 mmol) was condensed into a quartz vessel. At -50 °C the irradiation was carried out for 1 h. After collecting the crude reaction products in an external cooling trap, pure bis(undecafluoro-tert-pentyl) peroxide was obtained by trap-to-trap distillation (-45 °C / -78 °C / -196 °C) at -78 °C as a colorless solid (1.0 mmol, 50 %). The NMR and IR spectra match with those previously reported.[17] ¹³C(¹⁹F) DEPTQ NMR (neat, external [D₆]acetone, r.t.): δ [ppm] = 118.5 (C(CF₃)₂), 116.7 (CF₃), 115.2 (CF₂), 85.6 (CC₃). ¹⁹F NMR (CFCl₃, r.t.): δ [ppm] = -67.0 (m, 12F, C(CF₃)₂), -80.1 (m, 6F, CF₃), -115.6 (sept, 4F, ⁴J(F,F) = 12 Hz, CF₂). IR (gas): \tilde{v} [cm⁻¹] = 1340 (w), 1290 (s), 1277 (s, sh), 1269 (s), 1254 (vs), 1229 (s), 1187 (w), 1177 (w, sh), 1105 (s), 1086 (m), 1077 (m, sh), 1009 (w), 986 (m), 973 (m), 898 (s), 766 (w), 743 (s), 730 (s), 697 (vw), 656 (vw), 631 (w), 542 (w), 511 (w), 447 (vw). Raman (solid): \tilde{v} [cm⁻¹] = 1342 (m), 1289 (w), 1277 (s), 1245 (s), 1238 (w, sh), 1177 (vw), 1132 (m), 1125 (m, sh), 1082 (m), 1009 (w), 997 (w), 853 (s), 781 (vs), 766 (m), 751 (vs), 731 (vw), 686 (w), 657 (w), 632 (m), 596 (m), 566 (m, sh), 554 (m), 548 (m), 532 (mw), 449 (w), 373 (m), 352 (m), 332 (s), 323 (m, sh), 309 (m), 295 (s), 261 (w), 243 (s), 232 (m, sh), 199 (w), 117 (s). UV/Vis (gas): λ [nm] = 250.

Conflict of interest

There is no conflict of interest.

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