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No Fear of Perfluorinated Peroxides: Syntheses and Solid-State Structures of Surprisingly Inert Perfluoroalkyl Peroxides

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Abstract: *We report on the solid-state structures of bis(nonafluoro-tert-butyl) peroxide $[(F_3C)_3CO]_2$ and bis(undecafluoro-2-methyl-2-butyl) peroxide $[(C_2F_5)(F_3C)_2CO]_2$. These peroxides were prepared from the corresponding hypofluorites and fluorinated silver wool. The solid-state structures obtained after in situ crystallisation show unusual COOC dihedral angles of 180°, as well as elongated O–O bonds because of the bulky perfluorinated alkyl groups. The perfluorinated alkyl peroxides are insensitive to both impact (>40 J) and friction (>360 N), and resistant towards mineral acids (HX; X = F, Cl, Br) and elemental halogens (X_2). Ferrocene is oxidized by $[(F_3C)_3CO]_2$ to $[Fe^{III}Cp_2][OC(CF_3)_3]$.*

The introduction of fluorine into organic compounds often significantly modifies their physicochemical properties and their reactivity. Perfluorinated alkyl peroxides R^FOOR^F (**1**) are among those organic compounds about which our knowledge is rather limited thus far. This is surprising as they have been claimed to be synthetically valuable sources of fluorinated alkoxy radicals in a few previous studies,[1,2] and their non-fluorinated counterparts have been known for more than a century.[3] In 1858, Brodie discovered the first organic peroxides,[3] which nowadays are widely used in chemical synthesis and industrial processes, such as in oxidation and polymerisation reactions.[4,5] They also play an important role in atmospheric chemistry, for example, in ozone depletion.[6] The prototype dimethyl peroxide, $(H_3CO)_2$ (bp.: 14 °C), is formed in the stratosphere by oxidation of methane.[7] The versatile use of such peroxides as catalysts and activators is based on their selective O–O bond cleavage under formation of alkoxy radicals, which initiate chain reactions.[3,4] The cleavage of the peroxy bond in pure alkyl peroxides, which requires only a comparatively low thermal energy input and can also be easily initiated catalytically, often causes a very exothermic decomposition reaction, which may lead to an explosion or even detonation.[5] Liquid dimethyl peroxide has been reported to be shock-sensitive, and its vapour is subject to explosive decomposition.[7] However, as mentioned 60 years ago by Rieche,[3] the more large organic groups a peroxide bond is bound to, the more harmless it will be; and when a large and a small organic group are bound to a peroxide group, the larger one determines its temperament.

We have been interested in the properties of perfluorinated alkyl peroxides. Thus far, the most investigated perfluorinated alkyl peroxide is bis(trifluoromethyl) peroxide, $(F_3CO)_2$ (bp.: −37 °C). Its synthesis by treatment of carbonyl fluoride with elemental fluorine was reported in 1933 by Swarts[8] and later by Cady and co-workers.[9] Compared to $(H_3CO)_2$, it is surprisingly inert and thermally rather stable (up to 200 °C).[7] This very different reaction behaviour of the most simple dialkyl peroxides, $(H_3CO)_2$ versus $(F_3CO)_2$, cannot solely be attributed to their different bond dissociation energies. The O–O bond energy of dialkyl peroxides ROOR is about 160 ± 4 kJ mol^{-1} and almost independent of the nature of R,[7,10,11] while that of F_3CO–OCF_3 was estimated in two independent studies to be 193 ± 2[7] or 199 ± 2 kJ mol^{-1}.[11] The main difference in the decomposition behaviour of the two peroxides is due to secondary reactions of the initially formed alkoxy radicals, RO$^\bullet$. These are slow and endothermic for $(F_3CO)_2$ [Eq. (1)], but very fast

$$2\,F_3CO^\bullet \rightarrow F_3COF + F_2CO \qquad (1)$$

and strongly exothermic for the dimethyl analogue $(H_3CO)_2$ [Eq. (2)].[7]

$$2\,H_3CO^\bullet \rightarrow H_3COH + H_2CO \qquad (2)$$

More recently, the O–O bond dissociation energy of peroxides has been taken up again in several computational studies.[10–12]

Apart from $(F_3CO)_2$, the only perfluorinated alkyl peroxide that, to the best of our knowledge, has been studied thus far is the bis(nonafluoro-*tert*-butyl) peroxide, $[(F_3C)_3CO]_2$ (**1a**). It was first obtained among other by-products by Anderson and co-workers from the reaction of $(F_3C)_3COH$ with the very strong oxidizer chlorine trifluoride (ClF_3) in a high-pressure stainless-steal reactor.[13] It was later shown that also the low-temperature photolysis (200 W Hg lamp in a quartz reactor) of mixtures of perfluorinated *tert*-butyl hypofluorite, $(F_3C)_3COF$ (**2a**), with fluorine acceptors such as perfluorocycloolefins[14] or tetrafluorohydrazine (N_2F_4)[1] yielded the peroxide **1a**. The ^{19}F NMR spectrum (with a resonance at $\delta = -70.0$ ppm relative to internal $CFCl_3$) and the four strongest absorptions in the mid-IR spectrum of **1a** have been reported.[13] Its thermal decomposition was found to produce exclusively $(F_3C)_2CO$ and C_2F_6 with an activation energy of 149 ± 4 kJ mol^{-1}.[15,1] Surprisingly, only

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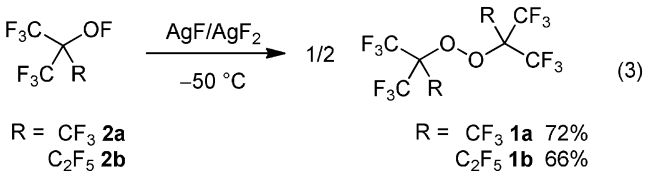
photochemical reactions of **1a** with perfluorocycloolefins have been studied thus far.[1] These earlier studies confirmed that **1a** can be used to transfer perfluorinated *tert*-butoxy groups to organic olefins.

Apart from the sparsely investigated photochemistry, the reactivity and structural properties of such bulky perfluorinated alkyl peroxides have remained largely unknown. We have developed a more convenient and safe synthetic access to these peroxides, which avoids the use of highly reactive chlorine trifluoride. In particular, we have revisited the reaction of known perfluorinated hypofluorites[16] **2** in the presence of various metal fluoride catalysts [Eq. (3)].[17]

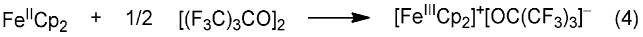


We finally found that perfluorinated alkyl peroxides such as **1a** and the hitherto unknown bis(undecafluoro-*tert*-pentyl) peroxide $[(C_2F_5)(F_3C)_2CO]_2$ (**1b**) can be conveniently obtained in yields of up to 72% by treatment of the hypofluorites $(F_3C)_3COF$ (**2a**) and $(C_2F_5)(F_3C)_2COF$ (**2b**), respectively, with fluorinated silver wool at −50 °C [Eq. (3); for experimental details see the Supporting Information]. At ambient temperature, these perfluorinated peroxides are rather inert colorless liquids. Solid **1a** melts at 18.4 °C, and its boiling point is reached under decomposition at 99.0 °C (see the Supporting Information).

We were intrigued whether these perfluorinated peroxides can undergo explosive decay and found that according to the UN recommendations, compound **1a** is rather insensitive to both impact (> 40 J) and friction (> 360 N).[18]

Owing to the low reactivity of these perfluorinated peroxides, they might be suitable as oxidation-resistant reaction media, for example, in halogenation reactions. We studied the reactivity of **1a** towards HF, HCl, and HBr upon heating to 70 °C. Mixtures of **1a** and anhydrous HF showed two liquid phases, but no reaction. While **1a** is stable towards HCl upon heating and irradiation in the gas phase, the nonfluorinated counterpart, di-*tert*-butyl peroxide, reacts with HCl vapour in a chain reaction involving free chlorine atoms.[19] We also found that **1a** did not react with elemental halogens such as F_2, Cl_2, or Br_2 at ambient temperatures. Even after irradiation or heating to 50 °C, **1a** remained unchanged in the presence of Cl_2 and Br_2. The low reactivity of this perfluorinated peroxide agrees with its computed electrostatic potential map shown in Figure S3.1. While the electrostatic potential of nonfluorinated di-*tert*-butyl peroxide suggests that the peroxy group is easily attacked by electrophiles, this group is well protected by the bulky perfluorinated alkyl groups in **1a** and **1b**.

As expected, perfluorinated peroxides are oxidants. Accordingly, DFT calculations at the B3LYP/aug-cc-pVTZ level of theory provided a rather large adiabatic electron affinity for **1a** of −373 kJ mol^{-1} (Table S3.2). Indeed, addition of ferrocene to liquid **1a** quantitatively yielded the ferrocenium nonafluoro-*tert*-butoxide [Eq. (4)]. The dark green solid product was well characterized by its characteristic IR spectrum (Figure S1.1), which shows the known vibrational modes for the $[Fe^{III}Cp_2]^+$ cation[20] and the alkoxide anion $[OC(CF_3)_3]^-$.[21]



The first solid-state structures of perfluorinated peroxides were obtained by in situ crystallisation at the diffractometer (Figure 1). Compound **1a** crystallizes at 283 K and compound **1b** at 270 K. Their structures were determined at 100 K where both compounds crystallize in the triclinic $P\bar{1}$ group

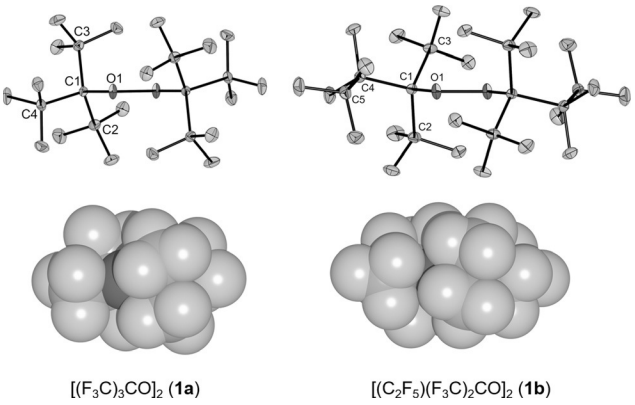


Figure 1. Single-crystal molecular structures of the perfluorinated bis(alkyl) peroxides **1a** and **1b** with thermal ellipsoids shown at the 50% probability level (top) and space-filling models (bottom).

(Table S2.1), with two molecules per unit cell for **1a**. They form columns along the *a* axis and layers along the *c* axis, with no significant intermolecular interactions (Figure S2.1). The shortest distance between the fluorine atoms of two neighbouring molecules of 297.8 pm is longer than twice the van der Waals radii (F: 147 pm[22]). Molecular structure parameters of **1a** and **1b** are summarized in Tables S2.2–S2.5. Some selected structure parameters of the fluorinated peroxides $(FO)_2$, $(F_3CO)_2$, and **1a,** and **1b** are compared in Table 1 to those of their nonfluorinated counterparts. One important feature of the molecular structures of **1a** and **1b** shown in Figure 1 is their *s-trans* conformation of the COOC backbone with a dihedral angle $\Theta = 180°$.

Regarding the molecular structure of some simple peroxides, there is a long-standing contradiction between experimental and computed gas-phase structures, which has been partially solved only very recently.[6,23,24] This concerns primarily the dihedral angle of these peroxides. Without interactions between the substituents at the peroxo unit, the COOC dihedral angle should be around $\Theta = 120°$. A dihedral angle of about 120° was only observed for the parent peroxide $(HO)_2$ (microwave (MW): $\Theta = 119.8(10)°$[6]) and the stable perfluorinated peroxide $(F_3CO)_2$ (gas-phase electron diffraction (GED): $\Theta = 123.3(4.0)°$[25]). The well-known skewed peroxide structure was rationalized as a compromise between

Table 1: Comparison of computed and experimentally obtained O–O bond lengths [pm] and XOOX dihedral angles Θ [°] for selected peroxides $(RO)_2$.

R	Exp. r(OO)	Exp. Θ	Exp. Ref.[a]	Calc. r(OO)	Calc. Θ	Calc. Ref.
H	145.2(5)	119.8(10)	MW[6]	145.3	122.5	[6, 26]
	146.1(3)	90.2(4)	XRD/ND[28]			
F	121.4(2)	88.1(4)	GED[29]	122.9	87.6	[24]
	121.7(5)	87.5(5)	MW[30]			
	118.6(2)	88.3(1)	XRD[31]			
H_3C	145.7(12)	135(5)[c]	GED[6]	145.9	180.0[c]	[23]
F_3C	141.9(20)	123.3(4.0)	GED[25]	144.3	124.3	[b]
$^tC_4H_9$	148[d]	165.8(2.4)	GED[27]	145.9	150.1	[b]
	147.8(3)	164.0(4)	XRD[32]			
$^tC_4F_9$	147.9(2)	180.0(5)	XRD[b]	146.2	180.0	[b]
$^tC_5F_{11}$	147.6(1)	180.0(1)	XRD[b]	146.2	178.4	[b]

[a] MW = microwave, XRD = X-ray diffraction, ND = neutron diffraction, GED = gas-phase electron diffraction. [b] This work (calculated at the B3LYP-D3BJ/def2-TZVP level of theory). [c] For more details, see the main text. [d] Fixed value.

several competing stereoelectronic effects (e.g., steric repulsion, electron pair repulsion, and orbital interactions).[6] Some simple peroxides such as $(HO)_2$,[6,26] $(FO)_2$,[24] and $(H_3CO)_2$[23] were shown to have non-rigid structures owing to an extremely flat potential energy minimum and/or large amplitude torsion modes. Their experimental gas-phase structures obtained either by rotational spectroscopy (e.g., MW: r_0 structure) or electron diffraction (GED: r_a structure) are derived from vibrationally averaged parameters. For such non-rigid molecules, the experimental r_0/r_a structure may differ significantly from a computed minimum structure, which in principle corresponds to the equilibrium structure of a molecule (r_e structure). As shown for $(HO)_2$,[6,26] $(FO)_2$,[24] and $(H_3CO)_2$,[23] a contradiction between an experimental and a computed structure was solved by computing vibrationally averaged structures. While the experimental gas-phase structure of $[(H_3C)_3CO]_2$[27] suggested a non-planar COOC backbone, a recent study confirmed that the computed r_e structure with an *s-trans* conformation of the COOC unit ($\Theta = 180°$) is indeed consistent with the previous experimental GED structure.

Molecular structures of the peroxides $(F_3CO)_2$, $[(H_3C)_3CO]_2$, and **1a** were calculated with different DFT and SCS-MP2 methods together with an augmented triple zeta basis (def2-TZVP; for computational details see the Supporting Information). These methods provided consistent structural parameters (see Table S3.1) similar to those previously reported for $(F_3CO)_2$ and $[(H_3C)_3CO]_2$.[11,33] In Table 1, B3LYP-D3BJ/def2-TZVP results are listed and compared to experimental values. While this method provides reliable estimates for the dihedral angles of these molecules, the O–O bond lengths, at least for the peroxides with bulky *tert*-butyl groups $[(H_3C)_3CO]_2$ (147.8(3) pm) and **1a** (147.9(2) pm), are slightly underestimated.

As mentioned above, one important feature of these peroxides is an extremely flat computed torsional potential, which exhibits either a very small *trans* barrier for $[(H_3C)_3CO]_2$ (see Figure S3.2) or a marginal *trans* minimum for **1a** (Figure S3.3). This general feature is due to competing and mutually balancing stereoelectronic effects.[6] The short O–O bond lengths in $(FO)_2$ are commonly explained by a stabilizing orbital interaction of the oxygen p-type lone pair with an antiperiplanar antibonding σ*(OF) orbital. Such an anomeric orbital interaction is favoured in the planar *s-trans* conformation of **1a**; however, its rather long O–O bond indicates considerable steric repulsion between the bulky perfluorinated *tert*-butyl substituents, well recognizable by the spherical model of **1a** shown in Figure 1 (bottom). On the other side, the computed C–O bond lengths (see Table S3.1) of the perfluorinated peroxides $(F_3CO)_2$ (138.9 pm) and **1a** (140.3 pm) are significantly shorter than those of the non-fluorinated analogues $(H_3CO)_2$ (142.0 pm)[23] and $[(H_3C)_3CO]_2$ (143.9 pm), which is consistent with a preferred anomeric interaction of the oxygen p-type lone pair with an antiperiplanar carbon-centred σ*(CX) orbital (X = F and CF_3, respectively).

The peroxide bond lengths (Table 1) correlate well with the dissociation energies for homolytic O–O dissociation: the longer the O–O bond lengths, the lower the bond dissociation energy. Bond dissociation energies (BDEs) computed at the DLPNO-CCSD(T) level of theory for selected peroxides are listed in Table 2. These values are up to 5% lower than those

Table 2: Comparison of O–O dissociation energies [kJ mol^{-1}] for the reaction RO–OR → 2 RO$^\bullet$ of different peroxides.

R	ΔE_{el}[a]	ΔG_{298} K[a]	BDE[b]	Exp.
F_3C	212 (179)	142 (109)	199 (167)	198.7 ± 2.1[11]
$^tC_4H_9$	186 (148)	114 (76)	170 (133)	179.6 ± 4.5[34]
$^tC_4F_9$	179 (125)	101 (46)	164 (109)	148.7 ± 4.4[15] [c]
$^tC_5F_{11}$	158 (97)	78 (18)	143 (83)	–

[a] Computed at the DLPNO-CCSD(T)/def2-QZVPP//B3LYP-D3BJ/def2-TZVP level of theory;[35] in parentheses: B3LYP-D3/def2-TZVP level of theory. [b] BDE(O–O) = $2\,H_{298}$(RO$^\bullet$) − H_{298}(RO–OR) at $T = 298$ K; $H = U + k_B T = E_{el} + E_{ZPE} + E_{vib} + E_{rot} + E_{trans} + k_B T$. [c] For deviation between experimental and calculated values, see the main text.

previously derived at the CBS-QB3 level from isodesmic and isogyric reactions;[10] however, they agree very well with the latest experimental values obtained for $(F_3CO)_2$[11] and $[(H_3C)_3CO]_2$[34] (Table 2). Earlier experimental activation energies determined from rate constants of the thermal decomposition of $[(H_3C)_3CO]_2$ (163 ± 2 kJ mol^{-1})[11] and **1a** (149 ± 4 kJ mol^{-1})[15] were questioned by a more recent photoacoustic calorimetry study, which recommended a higher BDE of 179.6 ± 4.5 kJ mol^{-1} for $[(H_3C)_3CO]_2$.[34] The low activation energy obtained for the thermal decomposition of these non-rigid *tert*-butyl derivatives might not be a good approximation for thermodynamic O–O bond energies, and a redetermination of the rather low experimental BDE for **1a** also needs to be considered (Table 2).

The photolysis of both $(F_3CO)_2$ and **1a** was used in previous studies to produce the synthetically valuable fluorinated F_3CO[1,2] and $(F_3C)_3CO$[1] radicals, respectively. We have recorded gas-phase UV/Vis spectra of these perfluorinated alkyl peroxides in the wavelength range 200–800 nm. In Figure 2, only the region up to 400 nm is shown. The lowest-energy transition of $(F_3CO)_2$ is below 200 nm[36] while **1a** and

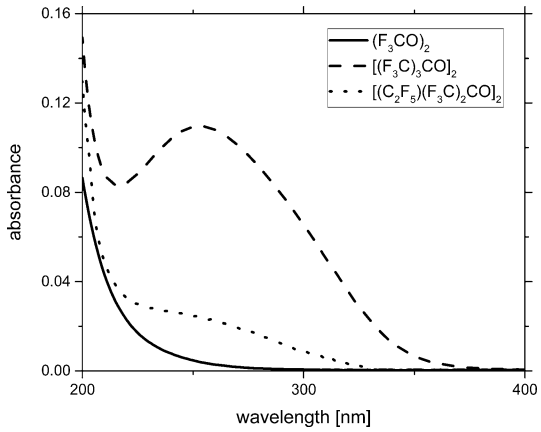


Figure 2. Gas-phase UV/Vis spectra (10 cm cell) of the perfluorinated bis(alkyl) peroxides $(F_3CO)_2$ (solid line, 50 mbar), $[(F_3C)_3CO]_2$ (**1a**, dashed line, 50 mbar) and $[(C_2F_5)(F_3C)_2CO]_2$ (**1b**, dotted line, 30 mbar).

1b show weaker red-shifted UV transitions at 253 and 250 nm, respectively. According to preliminary TD-DFT calculations (Table S3.2), these lowest-energy transitions almost exclusively correspond to HOMO–LUMO (n–π*) excitations. In agreement with previous studies,[34] the photodecomposition of **1a** using a 1000 W Xenon high-pressure lamp in a quartz vessel yielded quantitatively $(F_3C)_2CO$ and C_2F_6.

In conclusion, we have described safe syntheses of the perfluorinated peroxides **1a** and **1b** from the hypofluorites $(F_3C)_3COF$ (**2a**) and $(C_2F_5)(F_3C)_2COF$ (**2b**), respectively. Their solid-state structures feature rather long peroxide bonds and an unusual *s-trans* conformation along the COOC backbone with a dihedral angle of 180°. The molecular structures and O–O bond energies were compared to those of the nonfluorinated analogues. Their resistance towards oxidizing and halogenating reagents as well as their insensitivity to impact and friction make these liquid perfluorinated peroxides interesting solvents for halogenation reactions.

CAUTION! Safety note: Although the peroxides described were found to be insensitive to shock and friction[18] according to the UN Recommendations on the Transport of Dangerous Goods,[37] and although we have not observed any explosive decomposition during their handling, we cannot rule out that these compounds may react explosively when mixed with other substances.

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Keywords: fluorine chemistry · hypofluorites · molecular structure · peroxides · quantum-chemical calculations

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