area detector. Intensities were measured in the 2θ range 5–60°. Of a total of 33919 reflections, 6333 were independent ($R_{int} = 0.0468$). After absorption correction (multiple scan) the structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically against F^2 (G. M. Sheldrick, SHELXS-97, University of Göttingen, Göttingen (Germany), **1997**): $R_1 = 0.0222$, $wR_2 = 0.0630$ (all data). Methyl groups were refined as rigid groups, other hydrogen atoms by using a riding model. CCDC-175445 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

[17] R. T. Oakley, D. A. Stanislawski, R. West, *J. Organomet. Chem.* **1978**, *157*, 389–404; C. Couret, J. Escudie, J. Satgé, J. D. Andriamizaka, B. Saint-Roch, *J. Organomet. Chem.* **1979**, *182*, 9–15; W. Uhlig, *Z. Anorg. Allg. Chem.* **1990**, *588*, 133–138.

[18] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[19] M. Weidenbruch, S. Olthoff, K. Peters, H. G. von Schnering, *Chem. Commun.* **1997**, 1433–1434; A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, *Angew. Chem.* **1987**, *99*, 806–807; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 776–777.

[20] V. D. Romanenko, A. V. Ruban, S. V. Iksanova, L. K. Polyachenko, L. N. Markovski, *Phosphorus Sulfur Relat. Elem.* **1985**, *22*, 365–368.

[21] E. Seppälä, W.-W. du Mont, T. Gust, J. Mahnke, L. Müller, *1st Eur. Silicon Days* (München) **2001**, Abstract P27.

Fluoroformic Acid Anhydride, FC(O)OC(O)F**

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Dedicated to Professor Rüdiger Mews on the occasion of his 60th birthday

For many years new molecules, consisting only of fluorine, carbon, and oxygen atoms have been of fundamental interest.[1–10] The view that such species are formed in atmospheric degradation of HFCs and other CFC replacements[11,12] has motivated further work in this field.[13–16]

During our studies on radicals such as CF_3O,[17] CF_3OO,[18] $CF_3OC(O)$,[19] FCO_2[20], and FC(O)OO[18] that are important intermediates in the atmospheric degradation of CFC replacements, as well as on the catalytic oxidation of CO by CF_3O_x radicals,[21,22] we have also considered possible reaction products of these radicals, among them $CF_3OC(O)OC(O)OCF_3$.[17] Correspondingly, the formation of fluoroformic acid anhydride, FC(O)OC(O)F (**1**), by a recombination of FCO and FCO_2 radicals is considered in principle as feasible. However both radicals have to be present in sufficiently high concentrations for a satisfactory yield. We now report on the synthesis and characterization of **1**. This fundamental acid anhydride is, to our knowledge the first example of a XC(O)OC(O)Y species, with X,Y = halogen and can be viewed as halogen dicarbonate. It is at the same time the last missing member in the family of $FC(O)O_xC(O)F$ molecules ($x = 0$,[23] 1 (this work), 2,[1] 3,[24]), which had not previously been isolated in pure form.

The analogous, well known compound bis(fluoroformyl) peroxide, FC(O)OOC(O)F, is readily synthesized by the reaction of CO with a F_2/O_2 mixture; O_2, which must be present in large excess, acts as radical scavenger.[1,25–27] Accordingly, it was considered that using a 2:4:1 mixture of $F_2/CO/O_2$ may provide a suitable route for the synthesis of **1** according to reaction (1).

$$FCO + FCO_2 + M \rightarrow \mathbf{1} + M \quad (1)$$

However, since such mixtures tend to explode,[26] for the synthesis of FC(O)OOC(O)F experiments with lower concentrations of oxygen, which would lead to higher concentrations of FCO radicals, have been avoided. Our approach to synthesize **1** focuses on the thermal decomposition of FC(O)OOC(O)F in the presence of CO. Gaseous mixtures of FC(O)OOC(O)F and CO (1:5 to 1:10) are kept at 60 °C and the decay of the peroxide concentration is monitored by IR spectroscopy. We assume that the formation of **1** follows the reaction sequence given by Equations (2)–(4) then (1).

$$FC(O)OOC(O)F \xrightarrow{\Delta} 2\,FCO_2 \quad (2)$$

$$FCO_2 \xrightarrow{\Delta\Delta} F + CO_2 \quad (3)$$

$$F + CO + M \rightarrow FCO + M \quad (4)$$

The initial unimolecular decomposition of FC(O)OOC(O)F [Eq. (2)] is followed by a further unimolecular decomposition[20] [Eq. (3)] in which fluorine atoms are generated. These then react with CO to give FCO radicals [Eq. (4)]. In the final step FCO and FCO_2 radicals recombine to give the anhydride **1**, which is isolated from the reaction mixture after repeated trap-to-trap-condensation in vacuo. The gas-phase IR spectrum of **1** is depicted in Figure 1.

DFT calculations (B3LYP) with the 6-311 + G(d) basis set[28] predict the *syn–syn* conformer to be the most stable one for **1** (Figure 2). Calculated IR wavenumbers for this conformer are in good agreement with observed data (Table 1). By comparing observed and calculated band positions and

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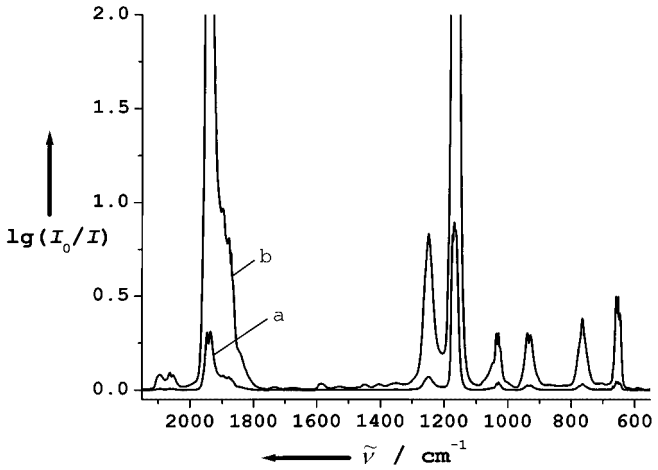

Figure 1. IR spectrum of **1** at 0.78 (a) and 7.95 mbar (b) (28 °C; optical length 19.5 cm).

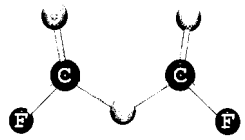

Figure 2. Structure of the most stable conformer of **1** (*syn–syn*) resulting from DFT calculations. Dihedral angles [°]: O=C-O-C 18.8, F-C-O-C 163.4; bond angles [°]: F-C-O 105.4, F-C=O 125.3, C-O-C 119.5; bond lengths [pm]: C-F 132.6, C-O 136.8, C=O 117.3.

intensities, the main absorption bands are attributed to the symmetric C=O (1941 cm^{-1}) and antisymmetric C-O-C (1168 cm^{-1}) stretching vibrations. The corresponding antisymmetric C=O and symmetric C-O-C vibrations are observed at 1870 and 938 cm^{-1}. The bands at 1249 and 1030 cm^{-1} are assigned as C–F vibrations.

The ^{19}F NMR spectrum shows a single signal at $\delta = -10.6$ and eight ^{13}C satellites (Table 2). The ^{13}C NMR spectrum exhibits besides a doublet for FC(O)OOC(O)F, which was used as solvent, a four-line signal for **1** which was centered at $\delta = 136.0$ ppm and thus is in a region, typical for a FC(O) moiety. The four lines in the ^{13}C NMR spectrum and the eight ^{13}C satellites in the ^{19}F NMR spectrum are consistent with the ABX spin system expected for the isotopologue $F^{13}C(O)O^{12}C(O)F$. An evaluation analogous to that for the ABX system of $F^{13}C(O)^{12}C(O)F$,[29] produces the coupling constants listed in Table 2. Comparing the ^{13}C NMR spectra of FC(O)C(O)F,[29] FC(O)OC(O)F, and FC(O)OOC(O)F[30] reveals that the presence of an increasing number of bonds between the NMR-active atoms results in a decreasingly resolved multiplet (X-part of the ABX system). ^{13}C and ^{19}F NMR data of $FC(O)OCF_3$, which also contains a FC(O)OC moiety, are very similar to those of **1**.

Gas density measurements yielded a value of 109.7 g mol^{-1} for the molar mass of **1**, which is in good agreement with the calculated value of 110.017 g mol^{-1}. The mass spectrum of **1** is also consistent with the expected fragmentation pattern for ionization at 70 eV (see Experimental Section). All findings strongly suggest that pure **1** was synthesized for the first time and that the IR bands observed in earlier experiments by Bednarek et al.[31] and Wallington et al.[32] appear to have been correctly assigned to **1**.

The UV spectrum (Figure 3) shows a structureless absorption band beginning at around 260 nm, similar to the band in FC(O)OOC(O)F[33] and FC(O)OOOC(O)F.[24] The values reveal that **1** is a poor UV absorber, which should be photostable in the troposphere.

Compound **1** condenses as a colorless liquid at 19.2 °C (extrapolated) and solidifies as a white solid at −46.2 °C (triple point). The synthesis gave yields between 15 to 30 % based on the conversion of FC(O)OOC(O)F. Side products are mainly COF_2, CO_2, SiF_4, and traces of two unidentified compounds with lower vapor pressures than **1.** The variation in yields depends on the condition of the surface of the reactor, since the decomposition of **1** is surface-catalyzed and

Table 1. Observed and calculated IR data of **1** in the gas phase.

$\tilde{\nu}_{exp.}$ [cm^{-1}]	$I_{rel.,exp.}$ [%]	$\tilde{\nu}_{calcd}$ [cm^{-1}][a]	$I_{rel.,calcd}$ [%][a]	Vibration (description)
1941	35	1985.5	54.4	ν_s(C=O)
1870	7	1909.9	10.5	ν_{as}(C=O)
1249	8	1230.9	6.1	ν_s(C–F)
1168	100	1143.0	100[b]	ν_{as}(C-O-C)
1030	5	1027.9	8.8	ν_{as}(C–F)
938	3	929.1	4.1	ν_s(C-O-C)
765	4	770.1	4.7	δ(FC(O)O)oop, i.p.
–	–	769.8	0.2	δ(FC(O)O)oop, o.p.
–	–	707.7	0.4	δ_s(FCO)
652	5	651.6	3.7	δ_{as}(FCO)

[a] B3LYP functional with 6-311 + G(d) basis set. [b] Absolute intensity: 1227 km mol^{-1}.

Table 2. ^{19}F and ^{13}C NMR data of FC(O)C(O)F, **1**, FC(O)OOC(O)F, and $FC(O)OCF_3$.

	FC(O)C(O)F	**1**[a]	FC(O)OOC(O)F	$FC(O)OCF_3$[b]
$\delta(^{19}F)$ (*F*CO)	+23.8	−10.6[c]	−34.1	−13.6
$^1\Delta^{19}F$[d]	−0.133	−0.120		
$^2\Delta^{19}F$[d]	−0.016	−0.001		
$\delta(^{13}C)$ (*F*CO)	+143.2	+136.0[e]	+142.3	+136.9
$^1J_{C,F}$ (*F*CO)	−366.3	−293.8	−301.1	295.1
$^2J_{C,F}$	+102.8			
$^3J_{C,F}$ (*F*C(O)O*C*)		+12.6		11.2
$^1J_{C,C}$	+126.1			
$^3J_{F,F}$	+50.6			
$\lvert^4J_{F,F}\rvert$		34.6		9.8
$\lvert^5J_{F,F}\rvert$			3.8	

[a] Measurements were carried out in CD_2Cl_2 at 223 K. Chemical shifts in ppm referenced to external $CFCl_3$ (^{19}F) and to CD_2Cl_2 at $\delta = 53.7$ ppm (^{13}C); coupling constants in Hz. [b] Ref. [17]. [c] ^{13}C satellite signals: −10.17, −10.29, −10.55, −10.60, −10.67, −10.73, −11.22, −11.35 ppm. [d] Isotopic shifts $\Delta = \delta(F^{13}C) - \delta(F^{12}C)$ of the ^{19}F resonance in ppm.[34] [e] ^{13}C multiplet (X-part of the ABX system): 138.1, 137.9, 134.1, 133.9 ppm.

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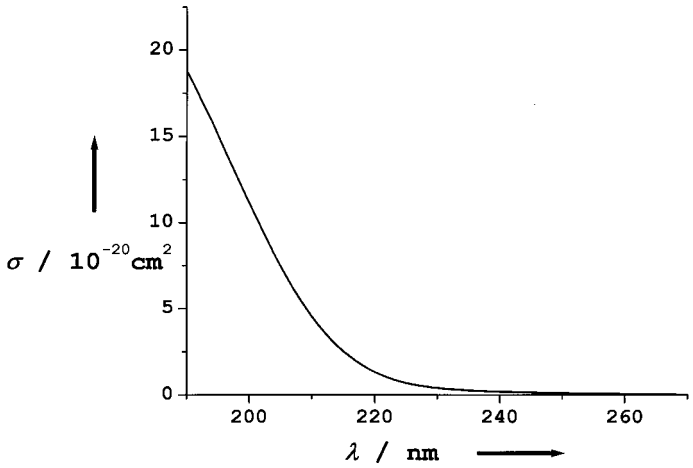

Figure 3. UV spectrum of **1**.

the compound reacts readily with moisture. After cleaning the reactor thoroughly and conditioning with FC(O)OOC(O)F, the yields of **1** are increased to 30%. In a glass IR cell with a well conditioned surface, **1** is stable at room temperature for several days. At 50°C **1** decomposes within hours to give COF_2, CO_2, and SiF_4.

Experimental Section

Caution: FC(O)OOC(O)F is potentially explosive if heated or brought in contact with oxidizable materials. It is recommended that appropriate safety precautions are thus taken when this compound is handled. Reactions involving FC(O)OOC(O)F should be carried out only in millimolar quantities.

1: In a typical reaction FC(O)OOC(O)F (ca. 2 mmol) and CO (20 mmol) were introduced into a clean, dry, and surface-conditioned (with 100 mbar FC(O)OOC(O)F, 1 h) 1-L glass bulb. This mixture was kept at 60°C until most of the FC(O)OOC(O)F had disappeared (ca. 4 to 6 hours; the progress of the reacion was monitored by IR spectroscopy). After cooling to −196°C and removal of the excess of CO in vacuo, the reaction mixture was separated by trap-to-trap-condensation (at −70, −120, and −196°C). Compound **1** was collected together with unreacted peroxide in the trap at −120°C. The −120°C fractions of several synthetic runs were collected and **1** was separated from the peroxide by evaporating the peroxide from the mixture at −95°C until a pure sample of **1** remained in the trap.

^{19}F NMR: 282.40 MHz, −50°C, $CFCl_3$; ^{13}C NMR: 75.47 MHz, −50°C, CD_2Cl_2.

MS (70 eV): *m*/*z* (%): 110 (1.5) [M^+], 85 (trace) [CF_3O^+], 69 (1) [CF_3^+], 66 (14) [F_2CO^+], 63 (trace) [FCO_2^+], 50 (1) [CF_2^+], 47 (43) [FCO^+], 44 (100) [CO_2^+], 33 (0.5) [F_2CO^{++}], 32 (2) [O_2^+], 31 (2) [FC^+], 28 (17) [CO^+ or N_2^+].

UV (gas): λ (σ in 10^{-20} cm^2 molecule^{-1}): 190 (18.79), 200 (11.14), 210 (4.54), 220 (1.32), 230 (0.40), 240 (0.19), 250 (0.11), 260 (0.05), 270 nm (0.02).

Vapor pressure curve (liquid phase): p [mbar], T [K], 274 K > T > 227 K: $\lg(p) = 9.767(0.015) - 1976.5(3.8)T^{-1}$.

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[1] A. J. Arvia, P. J. Aymonino, C. H. Waldow, H. J. Schumacher, *Angew. Chem.* **1960**, *72*, 169.
[2] R. L. Cauble, G. H. Cady, *J. Am. Chem. Soc.* **1967**, *89*, 5161.
[3] P. G. Thompson, *J. Am. Chem. Soc.* **1967**, *89*, 1811.
[4] E. L. Varetti, P. J. Aymonino, *J. Chem. Soc. Chem. Commun.* **1967**, 680.
[5] P. G. Thompson, *J. Am. Chem. Soc.* **1967**, *89*, 4316.
[6] D. D. DesMarteau, *Inorg. Chem.* **1970**, *9*, 2179.
[7] D. A. Couch, R. A. De Marco, J. M. Shreeve, *J. Chem. Soc. Chem. Commun.* **1971**, 91.
[8] D. Pilipovich, C. J. Schack, R. D. Wilson, *Inorg. Chem.* **1972**, *11*, 2531.
[9] F. A. Hohorst, D. D. DesMarteau, L. R. Anderson, D. E. Gould, W. B. Fox, *J. Am. Chem. Soc.* **1973**, *95*, 3866.
[10] A. Russo, D. D. DesMarteau, *Angew. Chem.* **1993**, *105*, 956; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 905.
[11] *Proceedings of the Workshop on the Atmospheric Degradation of HCFCs and HFCs* (Boulder, CO, USA, November 17–19 1993), AFEAS, Washington, **1993**..
[12] J. S. Francisco, M. M. Maricq, *Adv. Photochem.* **1995**, *20*, 79.
[13] S. I. Ahonkhai, A. Nölle, P. Behr, H. Heydtmann, *J. Photochem. Photobiol. A* **1994**, *80*, 389.
[14] J. S. Francisco, M. M. Maricq, *Acc. Chem. Res.* **1996**, *29*, 391.
[15] R. Meller, G. K. Moortgat, *Int. J. Chem. Kinet.* **1997**, *29*, 579.
[16] L. K. Christensen, T. J. Wallington, A. Guschin, M. D. Hurley, *J. Phys. Chem. A* **1999**, *103*, 4202.
[17] G. A. Argüello, H. Willner, F. E. Malanca, *Inorg. Chem.* **2000**, *39*, 1195.
[18] S. Sander, H. Pernice, H. Willner, *Chem. Eur. J.* **2000**, *6*, 3645.
[19] S. von Ahsen, J. Hufen, H. Willner, J. S. Francisco, *Chem. Eur. J.* **2002**, *8*, 1189.
[20] G. A. Argüello, H. Grothe, M. Kronberg, H. Willner, H.-G. Mack, *J. Phys. Chem.* **1995**, *99*, 17525.
[21] F. E. Malanca, G. A. Argüello, E. H. Staricco, *J. Photochem. Photobiol. A* **1997**, *103*, 19.
[22] F. E. Malanca, G. A. Argüello, E. H. Staricco, R. P. Wayne, *J. Photochem. Photobiol. A* **1998**, *117*, 163.
[23] N. Fukuhara, L. A. Bigelow, *J. Am. Chem. Soc.* **1941**, *63*, 788.
[24] H. Pernice, M. Berkei, G. Henkel, G. A. Argüello, T. R. Webb, M. L. McKee, H. Willner, unpublished results.
[25] J. M. Heras, A. J. Arvia, P. J. Aymonino, H. J. Schumacher, *Z. Phys. Chem.* **1961**, *28*, 250.
[26] A. J. Arvia, P. J. Aymonino, H. J. Schumacher, *Z. Anorg. Allg. Chem.* **1962**, *316*, 327.
[27] A. J. Arvia, P. J. Aymonino, *Spectrochim. Acta Part A* **1962**, *18*, 1299.
[28] Gaussian 98 (Revision A.5), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
[29] H. Pernice, H. Willner, R. Eujen, *J. Fluorine Chem.* **2001**, *112*, 277.
[30] H. Pernice, M. Berkei, H. Oberhammer, H. Willner, unpublished results.
[31] G. Bednarek, G. A. Argüello, R. Zellner, *Ber. Bunsen-Ges.* **1996**, *100*, 445.
[32] M. Goto, M. Kawasaki, T. J. Wallington, M. D. Hurley, A. P. Sharratt, *Int. J. Chem. Kinet.* **2002**, *34*, 139.
[33] M. M. Maricq, J. J. Szente, T. S. Dibble, J. S. Francisco, *J. Phys. Chem.* **1994**, *98*, 12294.
[34] W. Gombler, *J. Am. Chem. Soc.* **1982**, *104*, 6616.

  0044-8249/02/4120-3834 $ 20.00+.50/0