The reaction of dioxygenyl salts with ^{13}CO Formation of F^{13}C(O)^{13}C(O)F

Holger Pernice[a], Helge Willner[a,*], Reint Eujen[b,1]

[a]*FB6, Anorganische Chemie, Gerhard-Mercator-Universität Duisburg, Lotharstr. 1, D-47057 Duisburg, Germany*
[b]*FB9, Anorganische Chemie, Bergische Universität Wuppertal, Gaußstr. 20, D-42097 Wuppertal, Germany*

Abstract

Oxalyl fluoride has been prepared directly in high yield from CO and the dioxygenyl salts $O_2[BF_4]$ or $O_2[AsF_6]$. The formation of intermediate FCO radicals is indicated by differences in reaction rates and the observation of FC(O)OOC(O)F as a by-product. From the analysis of the NMR spectra of ^{13}C enriched FC(O)C(O)F including selective irradiation experiments positive signs for both the FF (+50.6 Hz) and CC (+126.1 Hz) coupling constants are deduced. From the temperature dependency of ^3J(FF), values of +70 Hz and −10 Hz are estimated for the *trans*- and *cis*-rotamers, respectively. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Since the discovery of the first dioxygenyl salt $O_2[PtF_6]$ by Bartlett and Lohmann [1], many other dioxygenyl salts containing the anions e.g. $[MF_6]^-$, M = P [2], As, Sb, Bi, Nb, Ta, Ru, Rh, Pd, Au [3,4], $[M_2F_{11}]^-$, M = Nb, Ta [3], Sb [3,5], $[MF_6]^{2-}$, M = Ni, Mn [6] and $[BF_4]^-$ [2] have been synthesized. They are conveniently prepared by photolysis of O_2/F_2 mixtures together with the respective Lewis acid [5,7] and characterized by vibrational spectroscopy [4–6,8], X-ray powder diffraction [1,5] and ESR spectroscopy [7]. The O–O stretching wavenumber is strongly dependent on the nature of the counter anion and spans from 1801 cm^{-1} in the $[O_2]_2[NiF_6]$ [6] to 1866 cm^{-1} in $O_2Ni[AsF_6]_3$ [8]. The crystal structures of $O_2[MF_6]$ salts with M = Sb, Ru, Pt, Au have been determined by single crystal X-ray diffraction [9]. But only recently a low temperature X-ray structure analysis of a $[O_2][RuF_6]$ single crystal [10] has proved the previously conjectured three-fold disorder of the O_2^+ cation in $[O_2][PtF_6]$ [11] and resulted in an interatomic O–O distance of 1.125 (17) Å in agreement with the gas phase value of 1.1227 Å [12]. The dioxygenyl cation is an one-electron

high-energy oxidizer and its chemistry has been exploited in solid salts or in aHF solution. It oxidizes xenon [13] and radon [14], and this property can be applied to remove radioactive gases from nuclear power plants and nuclear fuel reprocessing plants [15]. The O_2^+ salts also have been used to prepare salts of $C_6F_6^+$ [16], to oxidize HSO_3F to $S_2O_6F_2$ [17], isotopic enriched water to labeled ozone, $^*OO_2$, [18], and Ag(I), Ni(II), Au(III), Pt(IV) to $[AgF_4]^-$, $[NiF_6]^{2-}$, $[AuF_6]^-$, $[PtF_6]^-$, respectively [19]. In the latter case *in situ* generated O_2F dissolved in aHF was used as a vehicle for O_2^+ cations. O_2F radicals are also involved in the gas phase reaction system $O_2/F_2/CO$ which yields the peroxide FC(O)OOC(O)F [20]. This peroxide is an excellent thermal source for the synthesis of the unusual FCO_2 radical [21]. The determination of its molecular structure is at present under investigation [22]. In the course of these studies we became interested in the mechanism of the $O_2/F_2/CO$ reaction system, checked the reaction between carbon monoxide and dioxygenyl salts, and discovered that oxalyl fluoride is formed in high yield.

In general oxalyl fluoride is synthesized by fluorination of oxalyl chloride [23,24], but this route is not suitable for the preparation of isotopic enriched oxalyl fluoride. Hence, the above-mentioned new route enabled us to synthesize F^{13}C(O)^{13}C(O)F and to perform an extensive NMR study on this text book example for a $[AX]_2$ spin system [25,26].

* Corresponding author. Fax: +49-203-379-2231.
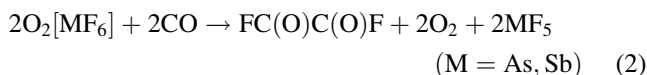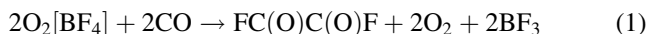*E-mail addresses*: willner@uni-duisburg.de (H. Willner),
eujen@uni-wuppertal.de (R. Eujen).
1 Co-corresponding author. Fax: +49-202-439-3052.

2. Results and discussions

2.1. Synthesis

Oxalyl fluoride has been prepared in high yields from carbon monoxide and a dioxygenyl salt in an one-step reaction according to
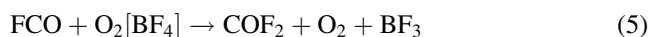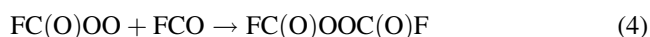
$$2O_2[BF_4] + 2CO \rightarrow FC(O)C(O)F + 2O_2 + 2BF_3 \qquad (1)$$

$$2O_2[MF_6] + 2CO \rightarrow FC(O)C(O)F + 2O_2 + 2MF_5$$
$$(M = As, Sb) \qquad (2)$$

The reaction rates of the heterogeneous reactions between the solid dioxygenyl salts and gaseous CO at ca. 200 mbar and $-60°C$ are very different. Reaction (1) is completed within 3–4 h, in the case of the $[AsF_6]^-$ salt (2) about 6 h are needed, and within 6 h only a few percent of the $[SbF_6]^-$ salt (2) is converted. Because the equimolar by-product AsF_5 is much more difficult to separate from oxalyl fluoride than BF_3, most experiments have been performed with the $O_2[BF_4]$ salt. In all cases COF_2 and $FC(O)OOC(O)F$ have been observed as side-products.

This new route to oxalyl fluoride is especially useful for the synthesis of isotopic labeled species and is applied in this study to the preparation of $F^{13}C(O)^{13}C(O)F$ for a subsequent comprehensive NMR investigation (*vide infra*). From the analytical point of view, IR spectroscopy is the easiest way to distinguish between natural and isotopic enriched oxalyl fluoride as demonstrated in Fig. 1.

It is of interest to elucidate the mechanism of reaction (1) and (2). The oxidizing strength of the O_2^+ cation (IP = 12.070 eV [27]) is too low to oxidize CO to the CO^+ cation (IP = 14.014 eV [28]), therefore formation of an intermediate like $[CO][BF_4]$ is not possible. Even formation of the possible dication $[OC–CO]^{2+}$ (isoelectronic to NC–CN) seems to be thermodynamically unfavorable. However,

synthesis and characterization of this simple dication may be a challenge for both experimentalists and theorists. Also formation of the intermediate cation $[OC–OO]^+$ can be ruled out, because after fluoride ion abstraction from the anion the $FC(O)OO$ radical [29] would be formed, which is the precursor for the peroxide $FC(O)OOC(O)F$ [20,30,31]. A good indication for the reaction mechanism stems from the reaction rate of the different dioxygenyl salts. The thermal stability of the salts $O_2[SbF_6]$, $O_2[AsF_6]$, $O_2[BF_4]$ decrease in this order due to an increase of the interionic interaction and preformation of the O_2F radical. Therefore, fluorine atom transfer to CO may occur on the surface of the dioxygenyl salts, and subsequent dimerization of the FCO radicals leads to $FC(O)C(O)F$. Side reactions of the FCO radicals with O_2 or the dioxygenyl salt give $FC(O)OOC(O)F$ or COF_2 according to

$$FCO + O_2 \rightarrow FC(O)OO \qquad (3)$$

$$FC(O)OO + FCO \rightarrow FC(O)OOC(O)F \qquad (4)$$

$$FCO + O_2[BF_4] \rightarrow COF_2 + O_2 + BF_3 \qquad (5)$$

If in the reaction vessel additional oxygen is introduced, the formation of $FC(O)OOC(O)F$ is increased and even the new trioxide $FC(O)OOOC(O)F$ is observed [32].

2.2. NMR spectra

The NMR spectra of ^{13}C enriched $FC(O)C(O)F$ represent a text book example for an $[AX]_2$ spin system with $A = {}^{19}F$ and $X = {}^{13}C$. The presence of the isotopomers $F^{13}C(O)^{12}C(O)F$ (15%, [ABX] spin system) and $F^{12}C(O)^{12}C(O)F$ (1%, $[A_2]$) in the investigated sample gives raise to additional lines. Due to distinct $^{13}C/^{12}C$ isotope shifts (Table 1) all expected 19 (10 + 8 + 1) lines are readily detected in the ^{19}F
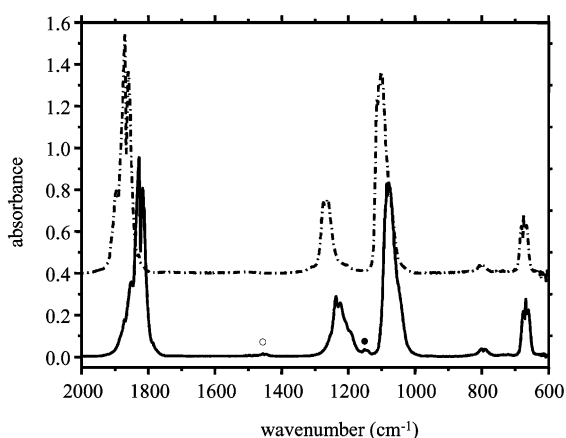

Fig. 1. IR spectra of 3.8 mbar natural (upper trace) and ^{13}C enriched oxalyl fluoride measured at 25 °C in a gas cell of 200 mm optical path length. The isotopic shifts for the bands at 1850, 1250, 1100, 800 and 670 cm^{-1} are 42.7, 38.2, 24, 4.7 and 6.3 cm^{-1}, respectively. Traces of BF_3 and $FC(O)OOC(O)F$ are indicated by (○) and (●), respectively.

Table 1
^{19}F and ^{13}C NMR data of $FC(O)C(O)X$ (X = F, Cl)[a]

	FC(O)C(O)F	FC(O)C(O)Cl
$\delta(^{19}F)$	+23.8	+15.7
$^1\Delta^{19}F(^{13/12}C)^{b,c}$	−0.133	−0.129
$^2\Delta^{19}F(^{12/13}C)^{b,c}$	−0.016	−0.013
$^1\Delta^{19}F(^{13/13}C)^{b}$	−0.148	−0.132
$\delta(^{13}C)$	+143.2	+145.0 (CF)
		+157.2 (CCl)[d]
$^1J(CF)$ (dJ/dT)[c]	−366.3 (−0.022)	−376.2 (−0.020)
$^2J(CF)$ (dJ/dT)[c]	+102.8 (0.018)	+96.7 (0.042)
$^1J(CC)$ (dJ/dT)[c]	+126.1 (0.002)	+112.9[e]
$^3J(FF)$ (dJ/dT)[c]	+50.6 (−0.068)	–

[a] In CD_2Cl_2 at 295 K. Chemical shifts in ppm refer to internal $CFCl_3$ (^{19}F) and to CD_2Cl_2 at 53.7 ppm (^{13}C). Coupling constants are in Hz; their temperature coefficients given in parentheses are in Hz K^{-1}.

[b] Isotopic shifts Δ of the ^{19}F resonance in ppm ($\delta(F^{13}C) - \delta(F^{12}C)$); for definition see [40].

[c] [33]: $^1J(CF)$ ±365.9 Hz, $^2J(CF)$ ∓103.2 Hz, $|^3J(FF)|$51.5 Hz, $^1\Delta^{19}F(^{13/12}C)$ −0.133 ppm, $^2\Delta^{19}F(^{12/13}C)$ −0.018 ppm.

[d] $\delta(^{13}C)$ $ClC(O)C(O)Cl$ 159.8 ppm.

[e] (dJ/dT) was not determined.
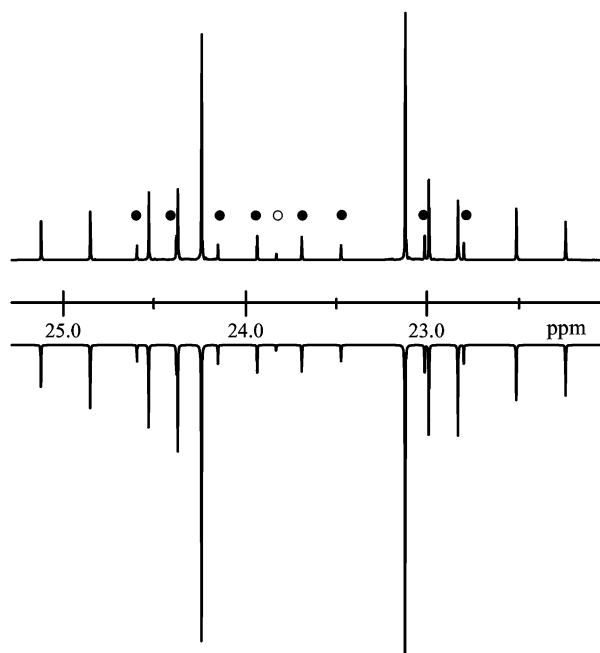
Fig. 2. Experimental (up) and simulated (down) ^{19}F NMR spectrum of F^{13}C(O)^{13}C(O)F recorded at 235.36 MHz. Signals marked with closed circles are due to F^{13}C(O)^{12}C(O)F (15%), the signal with the open circle is due to F^{12}C(O)^{12}C(O)F (1%).

Fig. 3. ^{13}C NMR spectrum of F^{13}C(O)^{13}C(O)F recorded at 62.90 MHz (upper trace). The lower trace shows the effect of selective irradiation of the lowest ^{19}F transition of the [AX]$_2$ system. Signals marked with closed circles are due to F^{13}C(O)^{12}C(O)F.

NMR spectrum, which is displayed in Fig. 2 along with a simulation. Isotope shifts are much smaller and not resolved in the ^{13}C NMR spectrum, and the two strongest lines of the ABX system are hidden by the central N lines of the dominating [AX]$_2$ system, while the "forbidden" ABX lines are very weak, but clearly visible close to the band center.

The absolute values of the one-bond and two-bond ^{13}C^{19}F couplings are directly accessible from the ABX system of F^{13}C(O)^{12}C(O)F and are in good agreement with the values reported by Bacon and Gillespie [33]. The opposite sign of these couplings, that is an indisputable negative ^1J(CF) and positive ^2J(CF) value, is confirmed by the distance of the N lines of the [AX]$_2$ spin system, $|^1J(\text{CF}) + ^2J(\text{CF})|$. Similarly, the ^3J(FF) coupling is evident from the ABX spin system while ^1J(CC) is obtained from the two AB sub spectra of the [AX]$_2$ system, the respective couplings being $K = |^1J(\text{CC}) + ^3J(\text{FF})|$ and $M = |^1J(\text{CC}) - ^3J(\text{FF})|$. Information about absolute signs of these couplings becomes available by selective irradiation experiments. Fig. 3 shows the effect upon irradiation of the ^{19}F transition which is lowest in energy and which forms part of one of the AB sub spectra of the ^{13}C^{13}C isotopomer. Those energy levels which are connected by the irradiated transition are split, thus those transitions which share one of these levels will also be split. Furthermore, the population of the respective levels is altered, e.g. saturation may lead to population inversion and negative peaks for regressive ($\Delta m = 0$) but intensification of progressive ($\Delta m = 2$) connections. In principal, the energy levels of an [AX]$_2$ spin system divide into a

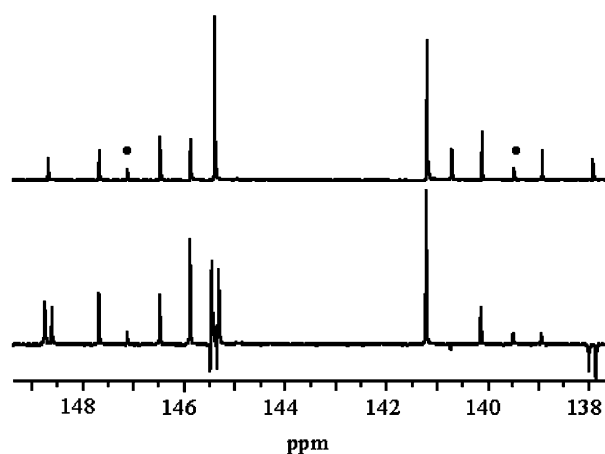symmetric part, containing the N lines and one AB sub spectrum, and an antisymmetric part with the second AB spectrum. Since one of the N lines is split (Fig. 3), the irradiated transition must belong to the symmetric part. If the adjacent line which belongs to the other AB sub spectrum is irradiated, the N lines are not affected. This implies that the ^1J(CC) and ^3J(FF) possess the same sign. A closer inspection of the spin system further reveals that the specific N line is only concerned if both signs are positive, yielding $^3J(\text{FF}) = +51$ Hz and $^1J(\text{CC}) = +126$ Hz. The results of the irradiation of the other ^{19}F transitions are in full agreement with the given assignment.

We have also studied the NMR spectra of the mixed fluoride chloride, FC(O)C(O)Cl. The relaxation times T_1 of the ^{13}C spins have been determined to be 31.5 and 41.5 s for ^{13}C(F) and ^{13}C(Cl), respectively. Observation of the ^{13}C satellites of the two ^{13}C resonances yields the one-bond coupling ^1J(CC). Its sign was determined by selective irradiation of the ^{19}F transitions of the corresponding ABX spin system which is very close to first order due to the large difference of the ^{13}C chemical shifts. The 4 X lines formed by the ^{13}C satellites of the ^{13}C satellites of the ^{19}F resonance line, while very weak, are clearly visible if recorded on neat or concentrated samples. Irradiation of the lowest ^{19}F frequency of the ^{13}C^{13}C isotopomer affects the low-frequency satellites of the ^{13}C resonances which is in accord with a positive sign for ^1J(CC).

Oxalyl fluoride exists as a mixture of two rotamers, a more stable *trans* form and a less stable *cis* form [34]. Based on the reported small enthalpy difference of 2.7 ± 0.6 kJ mol^{-1} along with the low rotational barrier of 10.9 ± 2.0 kJ mol^{-1} hen cooling down diluted solutions of FC(O)C(O)F or FC(O)C(O)Cl in CD$_2$Cl$_2$ from 295 to 213 K or 195 K, respectively, we could not observe a significant broadening of lines. Further cooling led to precipitation of the oxalyl halides. Since the values of shifts and coupling constants are

weighed averages of the respective values of the *trans* and *cis* isomers, there should be a slight but significant temperature dependence of those values which differ strongly. Inspection of the ^{19}F chemical shifts yields temperature coefficients of $+0.001$ ppm K^{-1} and $+0.016$ ppm K^{-1} for the difluoride and mixed halide, respectively. Similarly, the temperature dependence of the coupling constants (Table 1) albeit small is by far the largest for ^3J(FF). A low dependence is expected for the "fixed" couplings ^1J(CF), ^2J(CF) and ^1J(CC). In contrast, ^3J(FF) should be quite sensitive to the torsional angle. Inspection of literature data [36] reveals large differences for *cis* and *trans* couplings quite often connected with a change of the sign. For example, in fluorinated ethylenes the *cis* coupling is usually positive while the *trans* coupling adopts a large negative value, e.g. ^3J(FF$_{cis}$) $+73$ Hz and ^3J(FF$_{trans}$) -111 Hz for tetrafluoroethylene. On the other hand, a positive sign has been reported for ^3J(FF$_{trans}$) in CF$_3$CFCl$_2$ while the *gauche* coupling is negative. Similarly, positive *trans* and negative *cis* ^3J(FF) couplings have been observed in fluorinated cyclobutanes. Assuming that the intrinsic temperature dependence of the FF couplings of the isolated rotamers is negligible, a rough estimate of the *trans* and *cis* couplings in FC(O)C(O)F can be given. Based on the enthalpy difference of 2.7 kJ mol^{-1}, the amount of the *trans* isomer will increase from 75% at 295 K to 82% at 213 K which leads to an estimated $+70$ Hz for the *trans* and -10 Hz for the *cis* coupling.

3. Experimental section

Caution: *Fluorine, BF$_3$, AsF$_5$, and SbF$_5$ are very toxic and aggressive chemicals and they can cause severe burns. The experimentalist must become familiar with the safe handling of these reagents, before undertaking work as described here. Fresh tubes of calcium gluconate gel as well as cortisone ointment and spray should always be on hand for the fast treatment [37] of skin and respiratory tract exposed to these reagents.*

3.1. General procedures and reagents

Fluorine was measured by PVT and handled in a stainless steel vacuum line equipped with a capacitance pressure gauge (Model 205–2, 0–1700 mbar, Setra Acton, MA). Other volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (221 AHS-1000 and 221 AHS-10, MKS Baratron, Burlington, MA), three U-traps, and valves with PTFE stems (Young, London, UK). The vacuum line was connected to an IR cell (optical path length 200 mm, Si windows 0.5 mm thick) contained in the sample compartment of the FTIR instrument (Nicolet, Impact 400 D, Madison, WI). Gas-phase infrared spectra were recorded with a resolution of 2 cm^{-1} in the range of 4000–400 cm^{-1}. This set-up allowed

us to observe the reaction products and the purification processes immediately.

Air and moisture sensitive solids were manipulated inside an inert atmosphere box (Braun, München, Germany) flushed with argon, with a residual moisture content of less than 1 ppm. NMR measurements were carried out with samples, flame sealed in 5 mm o.d. tubes, with CD$_2$Cl$_2$ (Merck) as internal lock and a few % of CFCl$_3$ as reference.

The following gases were obtained from commercial sources and used after low temperature distillation: O$_2$ (Linde), F$_2$ (Solvay), CO (Linde), [13]CO (Deutero), BF$_3$ (Baker), AsF$_5$ (Baker). Liquid SbF$_5$ (Ozark-Mahoning) was used as received. FC(O)C(O)Cl was prepared according to a literature procedure [24] and stored in flame-sealed glass ampoules under liquid nitrogen in a long-term Dewar vessel. By using the "ampoule key" [38] the ampoules were opened on the vacuum line, an appropriate amount was taken out for the experiments and then they were flame-sealed again.

3.2. Synthetic reactions

The dioxygenyl salts were prepared by a modified literature procedure [5,7]. At the vacuum line an evacuated 250 ml glass bulb, fitted with a 10 mm valve having a PTFE stem (Young, London), was filled with 2.80 mmol BF$_3$, 2.40 mmol F$_2$, and 3.20 mmol O$_2$. The bulb was placed in a Dewar vessel containing a cold dry ice ethanol bath. The cold gas mixture was irradiated from top with UV-light of a 1000 W mercury high pressure lamp (type CS 1000W 2, Philips) for 1 h, and a white deposit was formed. The excess of O$_2$ and F$_2$ was pumped off at -196 °C, and after warming to -78 °C no volatile material could be detected. The mass of the bulb increased by 320 mg of O$_2$[BF$_4$] (96% yield). O$_2$[BF$_4$] is thermally unstable and it was used directly for the further reaction with CO. In a similar way O$_2$[AsF$_6$] was prepared in nearly quantitative yield, and the solid product was stored in the dry box. The synthesis of O$_2$[SbF$_6$] was performed according to the literature procedure [5].

The synthesis of the isotopic labeled F^{13}C(O)^{13}C(O)F was accomplished by the thermal reaction of O$_2$[BF$_4$] with ^{13}CO. Into the above-mentioned evacuated bulb containing 320 mg O$_2$[BF$_4$] (2.69 mmol) a small amount of 1.63 mmol ^{13}CO (1.63 mmol) was introduced at -196 °C. The remaining ^{13}CO in the vacuum line was recovered by cryopumping of the carbon monoxide into a vessel filled with molecular sieve (5 Å) held at -196 °C. Subsequently the reaction vessel was kept at -60 °C for 3.5 h. After cooling to -196 °C, formation of a non-condensable IR inactive gas (oxygen) and consumption of all ^{13}CO was recognized. By warming the bulb slowly to ca. 0 °C, all volatile products were evaporated and passed *in vacuo* through traps held at -120 and -196 °C, respectively. The trap held at -120 °C retained most of the F^{13}C(O)^{13}C(O)F contaminated with some F^{13}C(O)OO^{13}C(O)F, and at -196 °C some ^{13}COF$_2$ and BF$_3$ were trapped. By repeated fractional sublimation the product was purified and 44 mg of pure F^{13}C(O)^{13}C(O)F

(0.46 mmol, 56% yield) was isolated. With two more batches finally a total amount of 130 mg was prepared. The reactions between CO and $O_2[AsF_6]$ under the same conditions as described above was slower and needed about 6 h for completion. In the same time only a few percent of $O_2[SbF_6]$ was reacted.

3.3. NMR spectroscopy

Temperature dependent NMR spectra were obtained on a Bruker AC250 spectrometer operating at 62.90 or 235.36 MHz for ^{13}C or ^{19}F nuclei, respectively. Isotopic shifts were confirmed using a Bruker ARX400 spectrometer. The NMR signals were referenced using CD_2Cl_2 at 53.7 ppm and $CFCl_3$ as internal standards. Selective c.w. or pulsed ^{19}F irradiation was achieved using a second synthesizer connected to a power amplifier (Bruker BSV3BX).

The investigated NMR sample contained 100 mg $F^{13}C(O)^{13}C(O)F$ dissolved in 600 mg CD_2Cl_2 with 2 mol% $CFCl_3$ as internal ^{19}F standard. Due to the thermal properties of $FC(O)C(O)F$ [39], it crystallized at $-30\,°C$ from this solution. For studies at lower temperatures a sample containing ca. 5 mol% $F^{13}C(O)^{13}C(O)F$ in CD_2Cl_2 was used. The ^{13}C data for $FC(O)C(O)Cl$ were collected using an almost neat sample containing a small amount of the dichloride while temperature dependencies and chemical shifts were taken on a sample of ca. 5 mol% $FC(O)C(O)Cl$ and 1 mol% $CFCl_3$ in CD_2Cl_2.

Acknowledgements

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