

Preliminary communication

INSERTION OF SULFUR DIOXIDE INTO
 PERFLUOROALKYL-IRON BONDS

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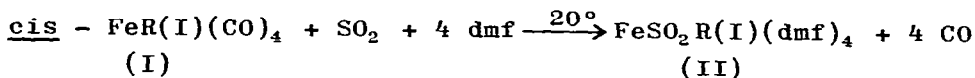
Summary

The reaction of perfluoroalkyl-iron(II) complexes, FeR(I)(CO)_4 ($\text{R} = \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_6\text{F}_{13}$), with SO_2 in dimethylformamide (dmf) leads to $\text{FeSO}_2\text{R(I)(dmf)}_4$. Characteristic features of this reaction are reported.

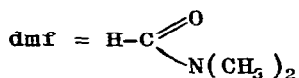
The sulfur dioxide insertion is known to be a facile process for many transition metal alkyls. SO_2 insertion has been suggested to arise mainly from an electrophilic backside attack of SO_2 at the α -carbon of a metal bonded alkyl group [1]. This is in contrast to the insertion of carbon monoxide which involves migration of the alkyl moiety to a carbonyl ligand.

However, perfluoroalkyl complexes are in general rather reluctant to undergo insertions and no such reaction with SO_2 has been observed so far.

We have now found that complexes of type I [2] react in dimethylformamide with excess SO_2 to give the perfluoroalkylsulfonates II under mild conditions.



(a: $\text{R} = \text{CF}_3$, b: $\text{R} = \text{C}_2\text{F}_5$, c: $\text{R} = \text{C}_6\text{F}_{13}$)



The rate markedly depends on R: while the reaction was complete after one day for Ic and after two days for Ib, only about ten percent of Ia had been transformed into IIa after four days. Products IIb (off-white) and IIc (ochre) were isolated by removing SO₂ and dmf at 0.1 torr as crystalline solids which are very sensitive to moisture and oxygen; product IIa was identified only vide infrared. Although conductivity measurements showed that the complexes II entirely dissociate in dilute dmf solutions, they probably contain the iodo-bridged dimers $[(\text{dmf})_4\text{FeI}_2\text{Fe}(\text{dmf})_4]$ (RSO₂)₂ in the solid state. This may be inferred from their analytical data combined with the presence of uncoordinated RSO₂ groups revealed by i.r. spectra.

As expected, chlorination with Cl₂ of II in water-dmf gave RSO₂Cl and alkylation with benzyl chloride led to benzyl perfluoroalkyl sulfones.

Interestingly, compounds II could also be obtained from 1-iodo-perfluoroalkanes, SO₂ and Fe(CO)₅, or even iron powder [5], in dmf.

In contrast to their behaviour in dmf the parent compounds I did not show any reaction with sulfur dioxide in liquid SO₂ or in a mixture of SO₂ and of n-hexane, at least not under moderate conditions. This suggested some direct interaction between I and dmf. Indeed, when samples of FeR(I)(CO)₄ were dissolved in dmf in the absence of SO₂, rapid evolution of carbon monoxide occurred. Volumetric gas determinations showed that two of the CO ligands were liberated at a very fast rate (15 min. with Ic and 30 min. with Ib) while loss of the remaining carbonyls was con-

TABLE 1
SOME TYPICAL INFRARED ABSORPTIONS OF FeSO₂R(I)(dmf)₄ II
(cm⁻¹, in nujol)

Compound	$\nu(\text{CF}) + \nu_{\text{as}}(\text{SO}_2)$	$\nu_{\text{s}}(\text{SO}_2)$
IIa	1170s, 1158s, 1122m	1020m
IIb	1217s, 1198m, 1155m	1019s
IIc	1241s, 1203s, 1174w 1148s, 1130w	1018m

siderably slower. Infrared spectra recorded after the initial phase, using Ib, exhibited three carbonyl bands at 2095 (m), 2045 (vs) and 1915 (m) cm^{-1} , the last one being due to bridging CO. Conductivity measurements which were performed 30 minutes after dissolving I gave values well within the range of typical binary electrolytes. It may be concluded from the above experiments that, at this stage, $[\text{FeR}(\text{CO})_2(\text{dmf})_3]\text{I}$ is the predominating species, whereas a carbonyl bridged dimer of unknown composition exists at much lower concentration. When SO_2 was present, formation of the bridged compound could be ruled out by i.r. inspection but, somewhat unexpectedly, no bands attributable to iron bonded sulfur dioxide could be detected.

To further clarify the situation, measurements of ^{19}F -n.m.r. spectra were attempted. Unfortunately these were unsuccessful in the cases of Ia and Ic because of strong paramagnetic line broadening. However, Ib gave well resolved spectra which in the absence of SO_2 indicated the formation of two major species in a ratio of about 7 : 1. The pattern of resonances observed with SO_2 was more complicated, but it gradually simplified and after two days consisted only of the two peaks expected for product Iib. It therefore is likely that SO_2 interferes at an early point of the reaction sequence, although the precise natures of the intermediates leading to the insertional product remain unclear.

TABLE 2

^{19}F -N.M.R. DATA OBTAINED WITH $\text{FeC}_2\text{F}_5(\text{I})(\text{CO})_4$ Ib ^a

Sample	$\delta(\text{CF}_2)$	$\delta(\text{CF}_3)$	Time after dissolution (h)
Ib, benzene- d_6	63.5	87.8	-
Ib, dmf ^b	68.3s, 75.9w	84.4s, 85.6w	0.6
Ib, dmf, SO_2	complex pattern		0.5
Ib, dmf, SO_2	81.8	77.8	48

^a Chemical shifts δ at 75 MHz, given in ppm upfield from CFCl_3 .

^b Shows also some very weak signals in addition to the reported ones.

Reactions of I with SO₂ similar to those described above for the dmf system were also observed using acetonitrile; however, both the displacement of CO by the solvent and the insertion of SO₂ were much slower than with dmf.

Conclusions and general implications

(i) The insertion reaction of FeR(I)(CO)₄ with SO₂ requires a polar solvent, e. g. dmf.

(ii) The first step consists of displacement of two CO ligands by solvent molecules to give cationic intermediates.

(iii) The displacement of π-acceptor carbonyl groups by "harder" σ-donating dmf ligands is likely to render the perfluoroalkyl-iron bond more polar, thus facilitating the SO₂ insertion.

Based on our results, it can be predicted that a variety of perfluoroalkyl complexes may undergo SO₂ insertion into the M-C bond under comparable conditions.

Acknowledgment

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References

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