Tetrahedron Letters,Vol.30,No.48,pp 6717-6720,1989   0040-4039/89 $3.00 + .00
Printed in Great Britain   Pergamon Press plc

MECHANISTIC STUDY ON THE PHOTOOXIDATION OF PERHALOFLUOROALKYL SULFINATES.

Chang-Ming HU, Ze-Qi XU and Feng-Ling QING

Shanghai Institute of Organic Chemistry, Academia Sinica,
345 Ling Ling Lu, Shanghai, People's Republic Of China.

Summary: Photochemical formation of methyl perhalofluorocarboxylates from the corresponding perhalofluoroalkyl sulfinates is considered to proceed via photochemical electron transfer.

In recent years, reactions based on fluoroalkyl sulfinates have been studied in detail [1]. Not only R_FSO_2Na can initiate the addition of R_FI[2] to double bond but also it can be used as a direct fluoroalkylating reagent to introduce a R_F group into certain olefinic compounds[3]. Pyrolysis of perfluoroalkyl sulfinates[4] and 3-oxa-perhalofluoroalkyl sulfinate[5] yielded perfluoroolefins and perhalofluorocarboxylic acids respectively. In previous papers[6,7], we reported that irradiation of perhalofluoroalkyl sulfinates with UV light afforded under mild conditions a simple and effective synthesis of perhalofluorocarboxylic acids and their esters in good yields (<u>scheme 1</u>)

$$R_FCXYSO_2Na \xrightarrow[H_2O \text{ or } MeOH,\ r.t.]{UV} R_FCO_2R$$

X, Y=F, Cl   R=H, when H_2O was used,
Me, when MeOH was used.

Scheme 1

Here we would like to describe a mechanistic study on the photochemical behaviour of these compounds. Sodium 3-oxa-11-chloroeicosafluoroundecane sulfinate [$Cl(CF_2)_8OCF_2CF_2SO_2Na$, 1] was taken as a model substance in this study.

All the reactions were run under the same conditions, i.e. MeOH(80ml), 500W high-pressure mercury lamp, quartz reaction tube and 5h irradiation at r.t. under air. The influence of additives on the distribution of products was shown in **Table 1**.

Photooxidation of 1 could not proceed through an anionic intermediate [$Cl(CF_2)_8OCF_2CF_2]^-$. As such anion was unstable, β-scission took place readily and $Cl(CF_2)_7CFO$ should be formed[5,8]. In the present case, however, no $Cl(CF_2)_7CO_2Me$ was detected.

1 was stable in the dark even at 45°C(entry 2). When the reaction was carried out under argon, only hydrogen abstraction product 3 was formed with a rather slow rate(entry 3). Since sulfinates have long been known as electron donors[2,3,9] and oxygen, an electron acceptor[10], thus these facts suggested that a photoche-

Table 1, Effect of Additives on the Photooxidation of 1

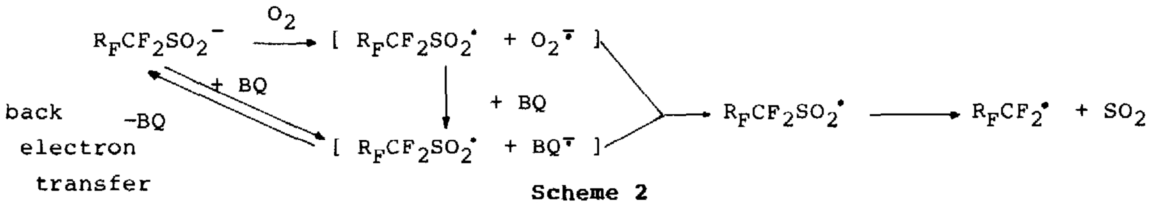
$$\underset{\underline{1}}{R_FCF_2SO_2Na} \xrightarrow{UV} \underset{\underline{2}}{R_FCO_2Me} + \underset{\underline{3}}{R_FCF_2H} + \underset{\underline{4}}{R_FCF_2SO_3H}$$

Entry	g(mmol) of 1	Solvent (ml)	Additive (mmol)	Composition of Products(%)[a]			
				1	2	3	4
1	2.5(3.91)	MeOH(80)	Air	----	100	----	----
2	2.5(3.91)	MeOH(80)	in the dark	100	----	----	----
3	2.5(3,91)	MeOH(80)	Argon	85	----	15	----
4	2.5(3.91)	MeOH(80)	p-DNB(1,01)[b]	26	65	----	9
5	2.5(3.91)	MeOH(80)	BQ(1.16)[c]	58	29	----	13
6	2.5(3.91)	MeOH(80)	NaI(1.0)	97	----	----	3

(a) The composition of products was determined by ^{19}F NMR.
(b) p-DNB: p-dinitrobenzene. (c) BQ: benzoquinone.

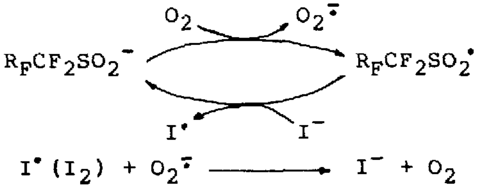
mical electron transfer from $R_FCF_2SO_2^-$ to oxygen might be involved and radical $R_FCF_2^\bullet$ was then formed.

Support for this hypothesis was adduced by carrying out the photoreaction in the presence of p-DNB (radical scavenger and electron transfer quencher) or BQ (efficient $O_2^{\bar{\bullet}}$ scavenger), both of which inhibited effectively the formation of carboxylate 2 (entry 4 and 5). The inhibition by p-DNB or BQ was achieved by the back electron transfer[11] as schemed in the following:



Scheme 2

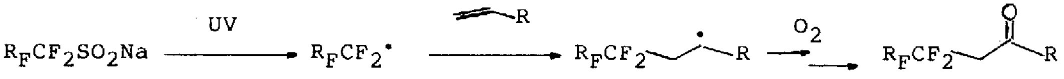
Further evidence for the electron transfer process was available if the experiment was conducted in the presence of NaI. It was found that the reaction was completely retarded under such conditions(entry 6). Such inhibition might be explained by electron transfer from I^-, an one-electron reductant[12], to radical $R_FCF_2SO_2^\bullet$ and by the reformation of I^- through an energetically favoured reaction[13] (**Scheme 3**).



Scheme 3

The intermediate $R_FCF_2^\cdot$ could be trapped by t-BuNO and detected by E.S.R.[14] A strong persistent and well resolved spectrum of the formed nitroxide, $t\text{-}BuN(O)CF_2R_F$, was obtained with a_N=11.54G and a_F^{β}=22.62G. Under argon, however, such nitroxide could not be detected by E.S.R.

It is noteworthy that if the reaction was carried out in the presence of n-hexene-1, a partially fluorinated ketone[15] was formed. Apparently such ketone was resulted from the addition of $R_FCF_2^\cdot$ to the double bond followed by oxidation.



Based on the foregoing results, a mechanism of photochemical formation of methyl perhalofluorocarboxylates from the corresponding sulfinates is presented in **Scheme 4**. Irradiation caused electron transfer from sulfinates to oxygen, and then the formed radical $R_FCF_2^\cdot$ yielded R_FCO_2Me through different ways.[16]

$$\begin{tikzcd}
\underset{\underline{\mathbf{1}}}{R_FCF_2SO_2^-} + O_2 \arrow[r, "UV"] & \underset{\underline{\mathbf{5}}}{R_FCF_2SO_2^\cdot} + O_2^{\cdot-} \arrow[r] \arrow[dr] & H_2O_2 \arrow[d] & (1) \\
& & HO^\cdot &
\end{tikzcd}$$

$$\begin{array}{rcll}
\underline{\mathbf{5}} & \longrightarrow & \underset{\underline{\mathbf{6}}}{R_FCF_2^\cdot} + SO_2 & (2) \\
\underline{\mathbf{6}} + O_2^{\cdot-} & \longrightarrow & \underset{\underline{\mathbf{7}}}{R_FCF_2O\text{-}O^-} & (3) \\
\underline{\mathbf{7}} & \longrightarrow & \underset{\underline{\mathbf{8}}}{R_FCF{=}O^+\text{-}O^-} + F^- & (4) \\
\underline{\mathbf{8}} & \longrightarrow & \underset{\underline{\mathbf{9}}}{R_FCFO} & (5) \\
\underline{\mathbf{7}} & \xrightarrow{H^+} & \underset{\underline{\mathbf{10}}}{R_FCF_2OOH} & (6) \\
\underline{\mathbf{6}} + O_2 & \longrightarrow & \underset{\underline{\mathbf{11}}}{R_FCF_2O\text{-}O^\cdot} & (7) \\
\underline{\mathbf{11}} & \xrightarrow{"H"} & \underline{\mathbf{10}} & (8) \\
\underline{\mathbf{10}} & \longrightarrow & \underline{\mathbf{9}} + HOF & (9) \\
\underline{\mathbf{6}} + HO^\cdot & \longrightarrow & \underset{\underline{\mathbf{12}}}{R_FCF_2OH} & (10) \\
\underline{\mathbf{12}} & \longrightarrow & \underline{\mathbf{9}} + HF & (11) \\
\underline{\mathbf{9}} + MeOH & \longrightarrow & R_FCO_2Me + HF & (12)
\end{array}$$

Scheme 4

REFERENCES

1a. W.Y.Huang, B.N.Huang and C.H.Hu, **J. Fluorine Chem.**, 23, 193(1983).

b. W.Y.Huang, J.L.Chen and L.Q.Hu, **Bull. Soc. Chim. Fr.**, 881(1986).

2. W.Y.Huang and J.L.Chen, **Acta Chimica Sinica**, 46, 669(1988).
3. W.Y.Huang, L.Q.Hu and Y.Xie, **Acta Chimica Sinica Engl. Ed.**, 190(1989).
4. C.Harzdorf, J.N.Meussdoerffer, H.Niederprum and M.Wechsberg, **Ann.**, 33(1973).
5. C.M.Hu, X.M.Du, H.F.Zhou, Z.Q.Xu and W.Y.Huang, **J.Fluorine Chem.**,37,377(1987)
6. C.M.Hu, Z.Q.Xu and W.Y.Huang, **J. Fluorine chem.**, 42, 145(1989).
7. C.M.Hu, Z.Q.Xu and W.Y.Huang, **Chinese J. Org. Chem.**, 8, 439(1988).
8. D.B.Su, Q.Y.Chen and R.X.Zhu, **Chinese J. Org. Chem.**, 112(1986).
9. A.E.Feiring, **J. Org. Chem.**, 50, 3269(1985).
10. P.S.Mariano and J.Stavinoha, **"Synthetic Organic Photochemistry"** ed.by W.M.Horspool, Plenum Press, New York, Chapter 3(1984).
11. H.D.Roth and M.L.Manion-Schilling, **J. Amer.Chem. Soc.**, 102, 4303(1980).
12. A.L.J.Beckwith and G.F.Meijs, **J.Org.Chem.**, 52, 1922(1987).
13. $$I^{\bullet}(I_2) + O_2^{\overline{\bullet}} \longrightarrow I^{-} + O_2$$
The free energy change of this process is given by the following equation and the electron transfer from $O_2^{\overline{\bullet}}$ to $I^{\bullet}$ or I_2 is thus calculated to be exothermic by about 35 kcal/mol.
$$\Delta G=23.6(E_{O_2^{\overline{\bullet}}/O_2} - E_{2I^{-}/I_2}) = -23.6(0.94 + 0.67) = -35 \text{ kcal/mole}$$
The data were taken from I.M.Kolthoff and J.F.Coetzee, **J. Amer. Chem. Soc.**, 79, 1852(1957); J.Eriksen and C.S.Foote, **ibid**, 102, 6083(1980).
14. Q.Y.Chen, Z.Y.Yang, C.X.Zhao and Z.M.Qiu, **J. Chem. Soc. Perkin Trans.1**, 563(1988).
15. The structure of $Cl(CF_2)_8OCF_2CF_2CH_2CO(CH_2)_3CH_3$ was elucidated by spectra and elemental analysis: C,29.80; H,1.81; F,58.59 (required: C,29.53; H,1.70; F, 58.39). **IR**(cm^{-1}): 1730. **MS:** 43(100, C_3H_7), 69(97.8, CF_3), 85(51.7, C_5H_9O), 634(34.9,M-16), 650(34.6,M). **^{19}F NMR**(neat): -9.2(2F,s,CF2Cl), 5.8(2F,s,CF_2O), 10.5(2F,s,CF_2O), 39.5(2F,t,J=18.8Hz,CF_2CH_2), 42.8(2F,s,CF_2), 44.2(8F,s,4CF_2), 48.0(2F,s,CF_2)ppm. **^{1}H NMR**(neat): 1.07(3H,t,J=4Hz,CH_3), 1.57(6H, m, 3CH_2), 2.83(2H,m,CH_2CF_2)ppm.
16a. S.C.Shim and J.S.Song, **J. Org. Chem.**, 51, 2817(1986).
b. K.Ishiguro, Y.Hirano and Y.Sawaki, **Tetrahedron Lett.**, 28, 6201(1987).

(Received in Japan 25 July 1989)