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PHOTOCHEMICAL FLUORINATION OF PERFLUOROPOLYETHER FUNCTIONAL DERIVATIVES

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SUMMARY

Oligomeric perfluorinated polyethers bearing various carbonylic end groups are reacted, at low or moderate temperatures, with fluorine under the influence of UV light. Carboxylic acylfluoride, and trifluoromethylketone groups are quantitatively cleaved under these conditions, while fluoroformate groups are mainly transformed into stable fluoroxy derivatives. Some mechanistic aspects of these photoreactions are discussed.

INTRODUCTION

One of the main technological problems in the manufacture of inert perfluoropolyether fluids is the final removal of their carbonylic and carboxylic functional end groups [1, 2, 3].

The penultimate products of the industrial manufacturing processes are in fact mixtures of perfluoropolyethers bearing at one end of the chain a ketone or an acyl fluoride group. To obtain a stable and inert product an end-capping treatment is required which is generally performed by reaction with fluorine at high temperature (i.e. over 200°C).

We have recently developed an end-capping process, based on a photochemical fluorination, much milder and easier to control than the thermal process [4].

During this work many aspects were examined on the reactions between fluorine and perfluorocarboxylic acids, acyl fluorides or

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ketones. Fluoroformates, R_fOCOF, showed an interesting reaction sequence.

This paper deals with the photochemical behaviour of these classes of compounds in a fluorine atmosphere. In order to obtain reliable information on the reaction features, low-molecular weight model compounds are employed as starting materials. The stability of perfluorinated chains makes the fluorination extremely selective toward the carbonylic position and consequently the structure of the products and their distribution are relatively easy to determine and interpret.

EXPERIMENTAL METHODS AND RESULTS

The U.V. extinction coefficients were measured with a Beckman 5270 spectrophotometer. The values for fluorine were taken from the literature [5]. The F_2 solubility in perfluoropolyethers was measured as 0.08 M at 25°C, 1 bar. The ^{19}F NMR spectra were recorded on a Varian 200 instrument with $CFCl_3$ as internal standard.

The fluorination experiments were carried out using cylindrical reactors with a inner double walled quartz well containing the lamp cooled with water or with a perfluorinated fluid (Galden D01). Elemental fluorine, after HF removal with NaF, was bubbled into the liquid without any dilution; however in the upper part (vapor phase) of the reactor, dilution with an inert gas was required for safety.

The radiation source was a standard Hanau T.Q.150 lamp with emission power of $4.95.10^{-5}$ E/s (einstein/sec) in the 238-354 nm range. The transmittance of the apparatus was assumed to be near 1 in every case.

The energy absorption was calculated assuming a cylindrical symmetry for the reactor, with the light coming from the central axis. The chromophore concentration, continuously decreasing with time, has been followed by G.L.C. or by acidimetric titration in order to evaluate the instant optical densities of the solution and finally the integral amount of light absorbed [6]. The concentrations of fluoroformates were best determined by NMR analysis.

The fluorination experiments were usually run without solvents or alternatively using a perfluorocarbon fluid as a solvent. The relatively high M.W. substrates, containing few reactive groups, did not require any special care for thermal control during reactions.

Carboxylic Acids Fluorination

A mixture of perfluoropolyether-acids having general formula $HO_2CCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2COOH$ of $\overline{M.W.} \simeq 2000$, n/m = 1.2, was fluorinated at 24°C in perfluoroheptane solution (30 g in 270 ml) with a F_2 flow rate 5 l/h for 8 hr. At the end of this time no more carboxylic groups were detectable in the liquid (I.R.). After solvent removal by distillation the residual liquid product, 27 g, was characterized by NMR: the ^{19}F signals of $-OCF_2COOH$ (-78.5 and -80.4 ppm) were replaced by $-OCF_3$ signals (-56.0 and -57.8 ppm). The OCF_3/OCF_2 ratio in the final product showed a M.W. very close to the starting one.

Acyl Fluoride Fluorination

The acyl fluoride $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF$ (500 g), obtained by trimerization of hexafluoropropene oxide, was fluorinated at 38°C under U.V. light for 18 hr with a F_2 flow rate of 10 l/h and an optical path of 18 mm.

The final product (390 g) was identified by mass spectroscopy and NMR as $C_3F_7OCF(CF_3)CF_2OCF_2CF_3$, the same described by Gerhard and Lagow [7]. In particular the three ^{19}F NMR signals of the

$-CF(CF_3)COF$ termination (-130.6, -82.3, +26 ppm) were replaced by the signals at -88.7 and -87.6 of the C_2F_5- group.

The low yield was due to losses by volatilization of both the reagent and the fluorinated product. After 16.5 hr of run time the light absorbed from the acyl fluoride was 1.67 E (calculated) while 0.31 E was absorbed from fluorine dissolved in solution. At the same time 0.97 moles of R_fCOF had been transformed. The values have been adjusted to correct for loss by evaporation. A quantum yield of ≃ 0.5 was estimated.

Ketone Fluorination

A mixture of perfluoropolyether-ketones $CF_3O(C_3F_6O)_n(CF_2O)_mCF_2COCF_3$, n/m = 20, was isolated from the perfluoropropene photoxidation products. A 344 g sample of this mixture, with a carbonyl content of 2.18 meq/g was fluorinated at 0°C under U.V. irradiation with a fluorine flow rate of 5 l/h and an optical path of 7 mm. During the reaction CF_3COF and minor amounts of COF_2 and CF_4 evolved. After 13 hr only traces of carbonyl groups were detectable. The yield was 240 g, some products were lost by volatilization.

The ^{19}F NMR signals at -75 ppm (CF_3CO- and $-CF_2CO-$) disappeared and the CF_3O- (-54 and -55.8) signals increased.

A quantum yield of 0.47 resulted from 0.60 moles of ketone transformed for 1.28 E of absorbed light. 1.19 E (calculated) are due to the ketone chromophore and 0.09 E to the fluorine dissolved in solution. The values have been estimated by adjusting for loss of evaporation.

Fluoroformate Fluorination

A mixture of perfluoropolyethers $X(CF_2O)_n(CF_2CF_2O)_mCOF$, $\overline{M.W.}$ 2500, n/m = 1.5, X = $-OCF_3$ or $-OCOF$ (30 g with 0.73 meq/g of fluoroformate) was dissolved in perfluoroheptane and fluorinated under U.V. light at -40 to -50°C. The optical path was 6.5 mm and the F_2 flow rate was 5 l/h.

After 22 hr there were no more detectable -OCOF groups in the solution. The weight of the final product, after solvent distillation, was 28 g. 18 meq of fluoroxy-groups (O-F) and 3 meq of peroxides (O-O) were formed. A total oxidizing power of 42 meq was found by iodometric titration. The $\overline{M.W.}$ increased to 2900 due to formation of the peroxide-bridges.

The amounts of functional groups and the molecular weights were evaluated by NMR.

The ^{19}F signals of the original and final functional groups are :

+154.5 (b),-69.6 (a) : $-OCF_2O\underset{a}{CF_2}O\underset{b}{F}$

+155.7 (b),-68.0 (a) : $-OCF_2CF_2O\underset{a}{CF_2}O\underset{b}{F}$

-12.2: $-OCF_2OCO\underline{F}$

-14.8: $-CF_2CF_2OCO\underline{F}$

-64: $-CF_2CF_2OC\underline{F}_2OO-$

-66: $-OCF_2OC\underline{F}_2OO-$ ppm from $CFCl_3$

DISCUSSION

The predominant reactions occurring in the fluorination process of the perfluoropolyethers (R_f = perfluoropolyether chain) can be summarized as follows:

$$R_fCOOH + F_2 \longrightarrow HF + CO_2 + R_fF \qquad (1)$$

$$R_fCOF + F_2 \longrightarrow COF_2 + R_fF \qquad (2)$$

$$R_fCOCF_3 + F_2 \longrightarrow CF_3COF + R_fF \qquad (3)$$

$$R_fCOCF_3 + F_2 \longrightarrow CF_4 + COF_2 + R_fF \qquad (4)$$

$$R_fCF_2OCOF + F_2 \longrightarrow R_fCF_2OCF_2OF \qquad (5)$$

$$R_fCF_2OCOF + F_2 \longrightarrow [R_fCF_2OCF_2OF] \longrightarrow R_fF + 2COF_2 \qquad (5b)$$

Reaction (5) has only been observed with high yields at very low temperatures (under -40°C).
For a complete end-capping of products containing fluoroformates it is necessary to carry out the photochemical fluorination at a somewhat higher temperature (reaction 5b).
Under the latter conditions COF_2 evolves and a fully end-capped product is obtained.
The main gaseous products observed during these fluorinations are COF_2 and CF_3COF. Minor amounts of CF_4 were detected in the off gases from the ketone fluorination.

The most reactive functional group among those considered, is the carboxy-group -COOH, the only one undergoing fluorination even in the absence of U.V. light at relatively low temperature.
The reactivities of the other functional groups toward fluorine have been evaluated by fluorinating, in photochemical conditions, a mixture of perfluoropolyethers of various functionalities; the rate of depletion of the different end-groups decreased in the following order :

$$-COCF_3 > -COF > -OCOF$$

Perfluorinated compounds with these functionalities are unreactive in the absence of U.V. under the experimental conditions, that is at relatively low temperature.

Both fluorine and perfluoroacylfluorides or ketones give activated species and then dissociate in the presence of U.V. light [8, 9, 10] :

$$F_2 \longrightarrow 2F^{\cdot} \qquad (6)$$

$$R_fCOF \longrightarrow R_f^{\cdot} + {}^{\cdot}COF \qquad (7)$$

$$R_fCOCF_3 \longrightarrow R_f^{\cdot} + CO + {}^{\cdot}CF_3 \qquad (8)$$

For a better understanding of the interrelations of events it is useful to compare the present process with the photodecomposition in the absence of fluorine.

The photodecomposition (or photocoupling) of perfluoroacylfluorides and ketones has been reported in the literature [11, 9] :

$$2R_fCOF \longrightarrow R_f - R_f + CO + COF_2$$

$$2R_fCOCF_3 \longrightarrow R_f - R_f + CO + CF_3 - CF_3$$

In Table 1 the extinction coefficients are recorded for the chromophores COF, $COCF_3$ and F_2.

TABLE 1

Extinction coefficients of some fluorocompounds at various wave-lengths.

$\epsilon = l \times mol^{-1} \times cm^{-1}$ λ = nm

λ	F_2	R_f(*)OCOF	R_f(*)COF	R_f(*)$COCF_3$
238	6.7	0.68	24.3	43.5
248	8.5	0.26	7.3	19.5
254	10.1	0.14	4.0	11.7
265	12.4	0.07	0.89	6.7
270	12.9	0.07	0.67	7.0
275	13.4	0.09	0.66	7.6
280	13.6	0.11	0.65	8.0
289	13.7	0.14	0.75	8.5
297	13.2	0.15	0.79	8.7
302	12.6	0.15	0.8	8.6
313	10.8	0.13	0.73	6.9
334	6.7	0.05	0.35	2.8
336	2.4	0.01	0.02	0.6
405	0.5	0.01	0.00	0.3

(*) R_f is a perfluoropolyether chain from C_3F_6 photoxidation and does not absorb U.V. light between 238-400 nm

Fig.1 and Table 2 illustrate the comparative data for the photofluorination and the photocoupling. The quantum yields refer to the total energy absorbed between the wave lengths 238 and 334 nm by the substrate and fluorine in solution. The quantum yields reported for the R_fCOF photocoupling are experimental values. The data are heterogeneous because of the different experimental conditions. Nevertheless, the quantum yield for the photofluorination of acylfluorides seems much higher and the overall reaction faster compared to the photocoupling.
The phenomenon suggests a higher efficiency for the fluorine molecules ultimately generating free radicals under U.V. irradiation.

A plausible scheme for the reaction steps is the following:

$$F_2 \xrightarrow{h\nu} 2F^{\cdot} \tag{9}$$

$$R_fOCFXCOX \xrightarrow{h\nu} (R_fOCFXCOX)^{*} \longrightarrow R_fOCFX^{\cdot} + {}^{\cdot}COX \tag{10}$$

$$(R_fOCFXCOX)^{*} + F_2 \longrightarrow R_fOCFXCFXO^{\cdot} + F^{\cdot} \tag{11}$$

$$R_fOCFXCOX + F^{\cdot} \longrightarrow R_fOCFXCFXO^{\cdot} \tag{12}$$

$$R_fOCFXCFXO^{\cdot} \longrightarrow R_fOCFX^{\cdot} + CFXO \tag{13}$$

$$R_fOCFX^{\cdot} + F_2 \longrightarrow R_fOCF_2X + F^{\cdot} \tag{14}$$

$$R_fOCFX^{\cdot} + F^{\cdot} \longrightarrow R_fOCF_2X \tag{15}$$

$$F^{\cdot} + F^{\cdot} \longrightarrow F_2 \tag{16}$$

$X = F;\ CF_3$

The radicals produced in reaction (11) can be in equilibrium with the corresponding fluoroxycompound:

TABLE 2

Quantum yields of photochemical reactions of perfluoroacylfluorides and ketones

Reaction conditions	Rf-COF M/E	$Rf\text{-}COCF_3$ M/E	Type of reaction
UV/Inert gas	0.1 (a)	-	End group cleavage and radical coupling
UV/F_2 5(h)	0.5 (c)	0.47 (c)	End group cleavage and fluorination

(a) Light intensity 1.57×10^{-5} E/s; Medium light path 13 mm.
(c) For conditions see experimental

The main energy absorption is by the C=O chromophore also in the photofluorination (see experimental). The results are consistent with a process of light assisted fluorine dissociation followed by radical chain propagation steps augmenting photochemical yields.

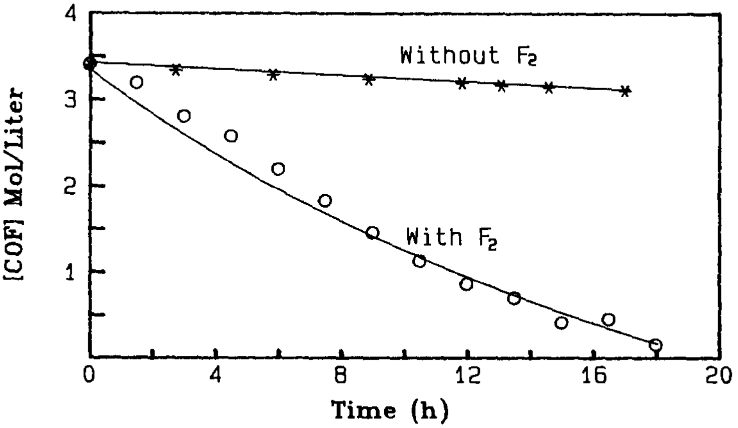
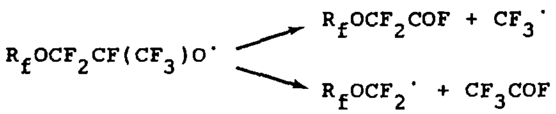


Fig. 1. Reaction trends of photocoupling and photofluorination experiments with $CF_3CF_2CF_2OCF(CF_3)CF_2OCF(CF_3)COF$ in UV light. Reaction conditions as reported in Table 2

$$R_fCOCFXCFXO^{\cdot} + F^{\cdot} \rightleftharpoons R_fOCFXCFXOF \qquad (17)$$

The reactions (12), (13) and (14) of the scheme can be considered as the chain propagation steps. They do not require radiant energy.

The ß-fission of the ketone-derived alkoxy radicals can pursue two different paths:



$$R_fOCF_2CF(CF_3)O^{\cdot} \rightarrow R_fOCF_2COF + CF_3^{\cdot}$$
$$R_fOCF_2CF(CF_3)O^{\cdot} \rightarrow R_fOCF_2^{\cdot} + CF_3COF$$

Both CF_4 and CF_3COF are present in the gaseous products. Acylfluorides can be detected in the early stages of the ketone fluorination process.

The formation of fluoroxycompounds (hypofluorites) proposed in reaction (17) has not been confirmed by isolation in the acylfluorides and ketones fluorination experiments. Acylfluoride and ketone-derived hypofluorites are well known and are quite stable at low temperature, however they are easily decomposed by U.V. light so that their presence would be only transient under photochemical conditions.

Fluoroformates show a different behaviour and in the presence of F_2 afford α-alkoxy-hypofluorites that are surprisingly stable to U.V. at low temperature

$$R_fOCOF + F_2 \xrightarrow{h\nu} R_fOCF_2OF \qquad (18)$$

The photochemical fluorination at higher temperature, e.g. over 50°C gives a complete removal of any functional group (including hypofluorites).

The easy isolation of the fluoroxycompounds derived from reaction (18) is due to the stability of the α-alkoxy substituted alkoxy radicals $R_fOCF_2O^{\cdot}$. They can react with fluorine to produce hypofluorites or recombine giving peroxides.

The fluoroformate-derived hypofluorites have been isolated for the first time in the present work [12]. Their presence indirectly supports the possibility that other hypofluorites are intermediates in these schemes.

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