

Available online at www.sciencedirect.com



Journal of Fluorine Chemistry 126 (2005) 633-639



www.elsevier.com/locate/fluor

Synthesis of α, ω -dimethoxyfluoropolyethers: reaction mechanism and kinetics

M. Avataneo*, U. De Patto, M. Galimberti, G. Marchionni*

Solvay Solexis R&D, Viale Lombardia 20, 20021 Bollate, Milan, Italy

Received 28 September 2004; received in revised form 21 January 2005; accepted 25 January 2005 Available online 25 February 2005

Dedicated to Prof. R.D. Chambers on the occasion of his 70th birthday.

Abstract

A new class of hydrofluoropolyethers, the α,ω -dimethoxyfluoropolyethers (DM-FPEs), characterized by the copolymeric structure CH₃O(CF₂CF₂O)_n(CF₂O)_mCH₃ has been recently developed. The synthesis of DM-FPEs here described, has been carried out via a new synthetic route which consists of the reaction of a perfluoropolyether diacyl fluoride with methyl fluoroformate in the presence of a metal fluoride. The reaction products are DM-FPEs and carbon dioxide.

Several reaction conditions has been tested varying type of solvent, temperature, type and amount of metal fluoride. The best results were obtained using tetraglyme as solvent and CsF as metal fluoride.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Dimethoxyfluoropolyethers; Hydrofluoropolyethers; Fluorinated fluids; Reaction rate; Methyl fluoroformate; Alkylation

1. Introduction

The α,ω -dimethoxyfluoropolyethers (DM-FPEs), having the copolymeric structure CH₃O(CF₂CF₂O)_{*n*}(CF₂O)_{*m*}CH₃ (where "*n*" and "*m*" indicate the content of the various moieties in the chain, whose distribution is random) are a new class of compounds recently developed by Solvay-Solexis. These chemicals are characterized by zero ozone depletion potential and by low global warming potential [1–6].

Several synthetic routes to hydrofluoroethers and hydrofluoropolyethers are known, such as fluorination of ether compounds [7–10], addition of alcohols to fluorinated olefins [11,12], alkylation of fluorinated alkoxides with a suitable alkylating agent (e.g. dialkylsulfate, alkyl-*p*toluensulfonate, alkyltriflate) [13] or with alkylfluorovinylethers [14], and finally catalytic alkylation of acylfluoride and ketones with Lewis acids and monofluoroalkanes [15]. The synthesis of DM-FPEs here described has been carried out via a new synthetic route which consists in the reaction of a perfluoropolyether diacyl fluoride with methyl fluoroformate in the presence of a source of fluoride ions, generally metal fluoride (MF) [16]:

$$R_{f}COF + CH_{3}OCOF \xrightarrow{\text{MIF}} R_{f}CF_{2}OCH_{3} + CO_{2}$$
(1)

.

The reaction products are DM-FPEs and carbon dioxide.

The selection of the best conditions for this reaction (Eq. (1)) is of primary importance for a possible application to industrial practice. In the present paper the effects of several reaction parameters on reaction rates are reported and discussed. A kinetic study is presented for the more promising reaction conditions.

2. Results and discussion

2.1. Synthesis of methyl fluoroformate

The methyl fluoroformate used in our experiments was prepared by bubbling, at low temperature (-65 ± 5 °C), an

^{*} Corresponding authors. Tel.: +39 02 3835 6672 (M. Avataneo)/+39 02 3835 6289 (G. Marchionni); fax: +39 02 3835 6355 (M. Avataneo)/+39 02 3835 2152 (G. Marchionni).

E-mail addresses: marco.avataneo@solvay.com (M. Avataneo), giuseppe.marchionni@solvay.com (G. Marchionni).

^{0022-1139/\$ –} see front matter \odot 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.jfluchem.2005.01.014

excess of carbonyl difluoride (COF_2) into a mixture of methanol and anhydrous sodium fluoride. The reaction products are methyl fluoroformate and hydrogen fluoride (Eq. (2)), that is rapidly scavenged by sodium fluoride (Eq. (3)):

 $COF_2 + CH_3OH \rightarrow CH_3OCOF + HF$ (2)

$$HF + NaF \rightarrow NaHF_2 \tag{3}$$

The conversion of methanol is complete and the molar yield in CH_3OCOF is higher than 95%. The only by-product detected is methyl carbonate, $CH_3OC(O)OCH_3$, which is formed by reaction of methyl fluoroformate with methanol (Eq. (4)):

$$CH_3OCOF + CH_3OH \rightarrow CH_3OC(O)OCH_3 + HF$$
 (4)

The relatively low yield of methyl carbonate can be explained considering the different reactivity of COF_2 and CH_3OCOF toward CH_3OH . The substitution of a fluorine atom with a methoxy group in methyl fluoroformate decreases the positive charge on the carbon of the carbonyl group, slowing down the reaction with methanol (Eq. (4)), especially at these low temperatures.

The difference of boiling points between methyl fluoroformate $(35 \ ^{\circ}C \ [17-20])$ and methyl carbonate $(90 \ ^{\circ}C)$ is high enough to enable, through a simple distillation, the recovery of the alkylating agent with a purity higher than 99% molar.

2.2. Synthesis of DM-FPEs

The perfluoropolyether diacyl fluorides (DAFs) having the structure

$FOCCF_2O(CF_2CF_2O)_p(CF_2O)_mCF_2COF$

are the starting reactant for the synthesis of DM-FPEs:

$CH_3O(CF_2CF_2O)_n(CF_2O)_mCH_3$

where p, m and n are well defined values indicating the content of the various moieties in the chain and n = p + 2.

The DM-FPEs are obtained by reacting, in a polar aprotic solvent, DAF (here indicated as R_fOCF_2COF to emphasize the acylfluoride end groups) with methyl fluoroformate and a metal fluoride (MF).

The reaction takes place trough the following two steps:

$$R_{f}OCF_{2}COF + MF \underset{k_{-1}}{\overset{k_{1}}{\xleftarrow{}}} R_{f}OCF_{2}CF_{2}O^{-}M^{+}$$
(5)

$$R_{f}OCF_{2}CF_{2}O^{-}M^{+} + CH_{3}OCOF \xrightarrow{k_{2}} R_{f}OCF_{2}CF_{2}OCH_{3} + CO_{2} + MF$$
(6)

In the first step (Eq. (5)) the acylfluoride group reacts with the metal fluoride to form the metal alkoxide $R_fOCF_2CF_2O^-M^+$ whose stability depends on the nature of the metal fluoride, on the temperature (an increase of temperature shifts the equilibrium to the left) [21] and on the type of solvent. In the second step (Eq. (6)) the alkoxide reacts with methyl fluoroformate leading to the introduction of a methoxy group at the end of the perfluoropolyether chain, to the formation of carbon dioxide and to the release of fluoride ion, which can react with another acylfluoride group.

The reaction system must be completely anhydrous to avoid the hydrolysis of the acyl fluoride group and the consequent formation of hydrogen fluoride. In the presence of MF, hydrogen fluoride forms MHF_2 which does not react with the acylfluoride to form the alkoxide. To avoid the generation of HF, the metal fluorides were thermally treated under nitrogen flow at 350 °C for at least 3 h and the solvents were stored in the presence of molecular sieves. DAF and methyl fluoroformate were also stored in the presence of sodium fluoride to scavenge the HF, possibly present, as NaHF₂.

The reactions of alkylation reported in the following paragraphs are described in details in Section 3.3.

2.2.1. Effect of solvents

Polar aprotic solvents are the most suitable for the synthesis of hydrofluoropolyethers and hydrofluoroethers when metal fluorides are required in the synthesis [13,16,22,23]. The solvents here investigated are tetraglyme, diglyme, acetonitrile, dimethylcarbonate, tetrahydrofuran, dimethylformamide, ethylene carbonate and methyl fluoroformate (this latter might act both as a solvent and as alkylating agent). They were all tested in the presence of cesium fluoride.

The rates of the two steps of the alkylation (Eqs. (5) and (6)) can be defined as:

$$\frac{d[R_{f}OCF_{2}CF_{2}OM]}{dt} = k_{1}[R_{f}OCF_{2}COF][MF] - k_{-1}[R_{f}OCF_{2}CF_{2}OM] - k_{2}[R_{f}OCF_{2}CF_{2}OM][CH_{3}OCOF]$$
(7)

$$\frac{d[R_fOCF_2CF_2OCH_3]}{dt} = k_2[R_fOCF_2CF_2OM][CH_3OCOF]$$
(8)

where k_1 and k_{-1} are respectively the direct and the reverse rate constant for the formation of the alkoxide $R_fOCF_2CF_2O^-M^+$ (Eq. (5)), k_2 is the rate constant for the reaction between the alkoxide and methyl fluoroformate (Eq. (6)).

According to Eqs. (7) and (8), the determination of the rate constants requires the measurement of the concentration of MF and R_fOCF_2COF during the reaction. But, being MF and R_fOCF_2COF in equilibrium with $R_fOCF_2CF_2O^-M^+$, the ¹⁹F-NMR spectra of the reaction mixture show, generally, only a single broad signal and, consequently, their concentration cannot be directly measured with this technique. Therefore, our first approach was to evaluate the effect of solvents only on the basis of the conversion, calculated from the ¹⁹F-NMR spectra, at different times.

Table 1 Effect of solvent on conversion (Boiling points of the solvents and reaction temperatures are also reported)

Solvent	Bp (°C)	Reaction temperature	Molar conversion (% of R _f OCF ₂ COF			
		(0)	1 h	2 h	3 h	4 h
Tetraglyme	276	75	22	31	40	48
Diglyme	162	75	6	9	10	11
Dimethylformamide	153	75	6	13	19	22
Dimethylcarbonate	90	75	0	0	0	0
Acetonitrile	82	65	0.5	1	1	2
Ethylene carbonate	244	55	4	6	8	_
Tetrahydrofuran	66	55	0	0	0	0
Methyl fluoroformate	35	30	0	0	0	0

The reactions were performed when possible at 75 °C, except for low boiling solvents such as acetonitrile, tetrahydrofuran, methyl fluoroformate, and for ethylene carbonate, which decomposes in the presence of fluorides at temperature above 70 °C (inorganic carbonates and CO_2 were observed). Reaction temperatures and conversions are reported in Table 1.

The highest conversions were obtained with tetraglyme (about 50% after 4 h) and this good result can be explained considering its coordinative effect toward metallic cations, which is similar to crown ethers [24,25]. Relatively high conversions were also obtained with diglyme, whose structure is similar to that of tetraglyme, and with dimethylformamide which is a highly polar solvent.

In the trial with tetraglyme the ¹⁹F-NMR spectrum of the reaction mixture showed, after a few minutes, two new narrow signals at -36 and -86 ppm which can be assigned respectively to $R_fOCF_2CF_2O^-Cs^+$ and $R_fOCF_2CF_2O^-Cs^+$. This indicates that the equilibrium 5 is completely shifted to the right ($k_1 \gg k_{-1}$) and that all the acylfluoride groups have been converted to cesium alkoxides. Using solvents which resulted in zero or near zero conversion (see Table 1), the ¹⁹F-NMR analyses evidenced only a broadening of the R_fOCF_2COF signal at +12 ppm: in this case the equilibrium 5 is shifted to the left ($k_1 < k_{-1}$) and the concentration of the alkoxide in the solution is presumably low.

When tetraglyme is used as solvent, all the acylfluoride is rapidly converted to alkoxide and its concentration can be directly measured via ¹⁹F-NMR (signals at -36 and -86 ppm). In this specific case, the reaction rate can be simplified as following:

$$\frac{d[R_{f}OCF_{2}CF_{2}OCH_{3}]}{dt} = -\frac{d[R_{f}OCF_{2}CF_{2}OM]}{dt}$$
$$= k_{2}[R_{f}OCF_{2}CF_{2}OM][CH_{3}OCOF]$$
(9)

and, if the concentration of CH_3OCOF is constant or can be considered constant (when it is used in large excess):

$$-\frac{\mathrm{d}[\mathrm{R}_{\mathrm{f}}\mathrm{OCF}_{2}\mathrm{CF}_{2}\mathrm{OM}]}{\mathrm{d}t} = K'[\mathrm{R}_{\mathrm{f}}\mathrm{OCF}_{2}\mathrm{CF}_{2}\mathrm{OM}]$$
(10)

where $K' = k_2$ [CH₃OCOF].

By integration between the initial time t_0 and the final time t, Eq. (10) becomes:

$$-\ln\left\{\frac{[R_{f}OCF_{2}CF_{2}OM]}{[R_{f}OCF_{2}CF_{2}OM]_{0}}\right\} = K't$$
(11)

where $[R_f OCF_2 CF_2 OM]_0$ is the concentration at the time t_0 . If the formation of the alkoxide is instantaneous:

$$\begin{split} & [R_f OCF_2 CF_2 OM]_0 = [R_f OCF_2 COF]_0, \\ & [R_f OCF_2 CF_2 OM] = [R_f OCF_2 COF]_0 - [R_f OCF_2 CF_2 OCH_3] \\ & \text{and Eq. (11) becomes:} \end{split}$$

$$-\ln\left\{\frac{\left[R_{f}OCF_{2}COF\right]_{0} - \left[R_{f}OCF_{2}CF_{2}OCH_{3}\right]}{\left[R_{f}OCF_{2}COF\right]_{0}}\right\} = K't$$
(12)

or

$$-\ln\left\{1 - \frac{[R_{f}OCF_{2}CF_{2}OCH_{3}]}{[R_{f}OCF_{2}COF]_{0}}\right\} = -\ln(1 - C)$$
$$= \ln\left(\frac{1}{1 - C}\right) = K't \quad (13)$$

where *C* is $\frac{[R_{f}OCF_{2}CF_{2}OCH_{3}]}{[R_{f}OCF_{2}COF]_{0}}$, i.e. the relative conversion. To summarize, Eqs. (11)–(13) are valid if:

- k₁ ≫ k₋₁, i.e. all the acylfluoride is rapidly converted to metal alkoxide.
- The initial concentration of $R_f OCF_2 COF$ is known.
- The concentration of R_fOCF₂CF₂O⁻M⁺ (or R_fOCF₂C-F₂OCH₃) at different reaction times is known.
- The concentration of CH₃OCOF is constant and known.

In Fig. 1 the plot of $ln(\frac{1}{1-C})$ versus reaction time for tetraglyme is reported. The concentrations of CH₃OCOF, R_fOCF₂CF₂OCH₃ and R_fOCF₂CF₂O⁻Cs⁺ were determined by means of ¹⁹F-NMR analyses (Ref. CFCl₃):

- CH₃OCO<u>F</u>: *δ* –19.0 ppm.
- R_fOCF₂<u>CF₂OCH₃: -94.4 ppm.</u>
- $R_f OCF_2 \underline{CF_2} O^- Cs^+$: -36 ppm.
- $R_fOCF_2CF_2O^-Cs^+$: -86 ppm.

The experimental points were fitted with a straight line whose slope is K'. Dividing K' by the concentration of CH₃OCOF a value of k_2 equal to $4 \pm 0.3 \times 10^{-5}$ l mol^{-mol-1} s⁻¹ was obtained (the molar concentration is relative to the end groups).

2.2.2. Effect of temperature

The effect of temperature was evaluated, using tetraglyme and CsF, in the range between +30 and +150 °C. At higher temperatures degradation was observed, probably due to the decomposition of methyl fluoroformate in the presence of metal fluoride.



Fig. 1. $\ln(\frac{1}{1-C})$, where *C* is the relative conversion, plotted as a function of the reaction time using CsF as metal fluoride and tetraglyme as solvent at 75 °C.



Fig. 2. $\ln(\frac{1}{1-C})$ reported as a function of the reaction time for different temperatures using CsF as metal fluoride and tetraglyme as solvent.

The graph of $\ln(\frac{1}{1-C})$ versus reaction time for all the trials is reported in Fig. 2. The experimental points are well interpolated by a linear equation ($R^2 > 0.97$) whose slopes were divided by [CH₃OCOF] to obtain k_2 .

The k_2 values, calculated at different temperature, are reported in Table 2. It is evident an increase of one order of magnitude every 20–30 °C increase of temperature. By introducing these data into the Arrhenius equation:

$$k = A \exp\left(\frac{-E_{\rm act}}{RT}\right) \tag{14}$$

i.e. by plotting $-\ln k_2$ as a function of 1/T (Fig. 3), an activation energy (E_{act}) of 17 kcal mol⁻¹ has been determined ($R^2 = 0.99$).

Table 2 Effect of temperature on the rate constant k_2 using CsF as metal fluoride and tetraglyme as solvent

Temperature (°C)	$k_2 \ (1 \ \mathrm{mol}^{-1} \ \mathrm{s}^{-1})$
30	$6\pm0.2 imes10^{-7}$
50	$6\pm0.5\times10^{-6}$
75	$4\pm0.3 imes10^{-5}$
110	$4\pm0.3\times10^{-4}$
150	$1\pm0.4 imes10^{-3}$



Fig. 3. Arrhenius plot for the reaction in tetraglyme as solvent and CsF as metal fluoride.

2.2.3. Effect of metal and organic fluorides

Fluorinated alkoxides can be prepared by reacting acyl fluoride with anhydrous compounds which can release fluoride ions. Among these, the metal fluorides are the most common even if organic compounds, such as phosponium salts or quaternary ammonium salts, have also been successfully employed for their higher solubility in the reaction media. In the present investigation, NaF, KF and CsF were tested in stoichiometric amount (molar ratio KF/R_fOCF₂COF = 1). In addition, the organic complex Et₃N·HF, whose use is reported in the literature for alkylation reactions on acylfluoride [26], was tested. The reaction conditions and the determined k_2 values are reported in Table 3.

At 50 °C CsF and KF present similar values of k_2 . As in case of CsF, the ¹⁹F-NMR spectra of the reaction mixture with KF show two narrow signals at -38 ppm ($R_fCF_2CF_2O^-K^+$) and at -86 ppm ($R_fCF_2CF_2O^-K^+$). No reaction product was observed with NaF and the ¹⁹F-NMR analyses show only a slightly broad signal of the acyl fluoride R_fCOF at +12 ppm (no significant formation of the alkoxide). These results can be interpreted in terms of the lattice energy of the salts, because the larger the lattice energy of the alkali metal fluorides, the more difficult is the formation of adducts [21]. The lattice energy of NaF (215 kcal mol⁻¹) is much higher than that of KF (192 kcal mol⁻¹) and CsF (176 kcal mol⁻¹) and the formation of the alkoxide by reaction with DAF is more difficult.

Also in case of Et_3N ·HF the degree of conversion was zero. Differently from NaF, the signal of acyl fluoride

Table 3

Effect of some metal and organic fluoride on the rate constant k_2 using tetraglyme as solvent

Fluoride Temperature (°C) k_2 (l mol ⁻¹ s ⁻¹ NaF 50 0 KF 50 $6 \pm 0.7 \times 10^{-1}$ CsF 50 $6 \pm 0.5 \times 10^{-1}$ [Et_3N·HF] 50 0 KF 110 $5 \pm 0.8 \times 10^{-1}$ CsF 110 $4 \pm 0.3 \times 10^{-1}$					
NaF 50 0 KF 50 $6 \pm 0.7 \times 10^{-1}$ CsF 50 $6 \pm 0.5 \times 10^{-1}$ [Et ₃ N·HF] 50 0 KF 110 $5 \pm 0.8 \times 10^{-1}$ CsF 110 $4 \pm 0.3 \times 10^{-1}$	Fluoride	Temperature (°C)	$k_2 \ (1 \ \text{mol}^{-1} \ \text{s}^{-1})$		
KF 50 $6 \pm 0.7 \times 10^{-1}$ CsF 50 $6 \pm 0.5 \times 10^{-1}$ [Et_3N·HF] 50 0 KF 110 $5 \pm 0.8 \times 10^{-1}$ CsF 110 $4 \pm 0.3 \times 10^{-1}$	NaF	50	0		
CsF 50 $6 \pm 0.5 \times 10^{-1}$ [Et_3N·HF] 50 0 KF 110 $5 \pm 0.8 \times 10^{-1}$ CsF 110 $4 \pm 0.3 \times 10^{-1}$	KF	50	$6\pm0.7 imes10^{-6}$		
$[Et_3N\cdot HF]$ 50 0 KF 110 $5 \pm 0.8 \times 10^{-1}$ CsF 110 $4 \pm 0.3 \times 10^{-1}$	CsF	50	$6\pm0.5\times10^{-6}$		
KF 110 $5 \pm 0.8 \times 10^{-1}$ CsF 110 $4 \pm 0.3 \times 10^{-1}$	[Et ₃ N·HF]	50	0		
CsF 110 $4 + 0.3 \times 10^{-1}$	KF	110	$5\pm0.8 imes10^{-5}$		
	CsF	110	$4\pm0.3\times10^{-4}$		

R_fOCF₂COF at +12 ppm disappeared and a new very broad signal appeared at about -60 ppm (the base of the signals covers a range of about 40 ppm). This seems to be indicative of a partial conversion of the acylfluoride to the alkoxide. The low concentration of the alkoxide together with the steric hindrance of the counterion Et₃NH⁺ could explain the difficulty of the reaction with methyl fluoroformate. To confirm the presence of the alkoxide another experiment was carried out with Et₃N·HF using the same reaction conditions except for the alkylating agent. By substituting the methyl fluoroformate with a more reactive alkylating agent, the methyl paratoluensulfonate, all the acyl fluoride end groups were converted to R_fCF₂CF₂OCH₃ in less than 30 min, confirming the existence of $R_f CF_2 CF_2 O^- Et_3 NH^+$. The reactivity of Et₃N·HF is intermediate between NaF and CsF and requires an alkylating agent more reactive than methyl fluoroformate.

KF and CsF were also tested at 110 °C. At this temperature a moderate difference of reactivity was observed between the two salts, being the value of k_2 of CsF about eight times higher than that of KF.

To increase the rate of alkylation, the trial with KF in tetraglyme at 50 °C was repeated in the presence of dibenzo-18-crown-6-ether (2.5% of the molar amount of KF). This crown ether strongly interacts with the potassium cation whereas the fluoride anion remains free and might react more easily with the acylfluoride. However, no noticeable variation of the reaction rate was observed and this could probably be explained taking into account the effect of the solvent tetraglyme which, acting in the same way as a crown ether, could hide the effect of the crown ethers.

2.2.4. Effect of the amount of metal fluoride

For Eqs. (11)–(13) we have assumed that the equilibrium between MF and $R_f OCF_2 COF$ is completely shifted to right, i.e. $k_1 \gg k_{-1}$. If this is true, the equilibrium should not be appreciably affected by the variation of the concentrations of the acylfluoride and of the metal fluoride and, when the concentration of the metal fluoride is lower than its stoichiometric value, we can write:

$$[\mathbf{R}_{\mathbf{f}}\mathbf{O}\mathbf{C}\mathbf{F}_{2}\mathbf{C}\mathbf{F}_{2}\mathbf{O}\mathbf{M}]_{0} = [\mathbf{M}\mathbf{F}]_{0} \tag{15}$$

Some tests were carried out to confirm that $k_1 \gg k_{-1}$. In these tests the molar ratio KF/R_fOCF₂COF was varied from 0.75 to 0.13 and ¹⁹F-NMR analyses of the reaction mixture were performed in the range of conversion between 0 and 15% molar. If $k_1 \gg k_{-1}$, in this range of conversions:

$$[\mathbf{R}_{f} \mathbf{O} \mathbf{C} \mathbf{F}_{2} \mathbf{C} \mathbf{F}_{2} \mathbf{O} \mathbf{M}] = [\mathbf{M} \mathbf{F}]_{0} = \text{constant}$$
(16)

and, if the concentration of CH_3OCOF is constant, the alkylation rate is constant too:

$$\frac{d[R_{f}OCF_{2}CF_{2}OCH_{3}]}{dt} = k_{2}[R_{f}OCF_{2}CF_{2}OM] \times [CH_{3}OCOF]$$
$$= constant$$
(17)

Table 4 Effect of the amount of KF on the rate constant k_2 at 50 °C using tetraglyme as solvent

Amount of KF ^a	$k_2 \ (l \ mol^{-1} \ s^{-1})$
1.00	$6\pm0.7\times10^{-6}$
0.75	$6\pm0.2 imes10^{-6}$
0.50	$7\pm0.2 imes10^{-6}$
0.38	$7\pm0.1 imes10^{-6}$
0.25	$6\pm0.1 imes10^{-6}$
0.13	$5\pm0.2 imes10^{-6}$

^a Molar ratio KF/R_fOCF₂COF at time zero.

By plotting the concentration of $R_fOCF_2CF_2OCH_3$ versus the reaction time straight lines were obtained. Their slopes, divided by [$R_fOCF_2CF_2OM$] and by [CH_3OCOF], give the k_2 values.

In Table 4 the amounts of KF are reported together with k_2 . As we can see, there is a narrow variation of the calculated values of k_2 with the amount of metal fluoride: this confirms that k_1 is much higher than k_{-1} .

3. Experimental

DAFs are not commercially available products and they were synthesized according to the below reported description. Carbonyl difluoride were purchased from Apollo Scientific Ltd. whereas all the other reagents were purchased from Aldrich Chemical Co.

3.1. Synthesis of DAFs

DAFs can be obtained in a two steps process. The first (Eq. (18)) includes the oxidative polymerization of tetrafluoroethylene at low temperature in a suitable fluorinated solvent. Elemental fluorine or UV light are used to generate radicals [27–29]. A peroxide polymeric precursor is formed as a result of the polymerization reaction:

$$CF_{2} = CF_{2} + O_{2}$$

$$\xrightarrow{\text{fluorine or UV}}_{<-40 \text{ }^{\circ}\text{C,solvent}} \text{TO} - (CF_{2}CF_{2}O)_{q} - (CF_{2}O)_{r} - (O)_{s} - T'$$
(A)
(18)

whose constituents are fluoroether repeating units $(-CF_2CF_2O- \text{ and } -CF_2O-)$ interspersed with peroxy units $(-CF_2CF_2OO- \text{ and } -CF_2OO-)$. The end groups T and T' are perfluorinated $(-CF_3 \text{ and } -CF_2CF_3)$. Compositions of the polymer and reaction yields (>90% molar) depend on temperature and TFE concentration. Carbonyl difluoride and tetrafluoroethylene oxide are the main by-products.

The peroxy groups of the perfluoropolyether-polyperoxide (\mathbf{A}) can be cleaved by reaction with hydrogen over a suitable catalyst to yield substantially bifunctional acyl fluorides [30]:

$$(\mathbf{A}) + \mathbf{H}_{2}$$

$$\stackrel{\text{Pd catalyst}}{\underset{100-200 \,^{\circ}\mathbf{C}}{\overset{\text{Pd CCF}_{2}\mathbf{O}-(\mathbf{CF}_{2}\mathbf{CF}_{2}\mathbf{O})_{p}(\mathbf{CF}_{2}\mathbf{O})_{m}-\mathbf{CF}_{2}\mathbf{COF}}{(\mathbf{B})}$$

$$(19)$$

3.2. Synthesis of methyl fluoroformate

An amount of 80 g of carbonyl difluoride was gradually bubbled in a mixture of 45 g of NaF (dried at 320 °C under high vacuum for 3 h) and 30 g of methanol previously charged in a 100 ml three necked glass flasks equipped with a stirring bar. The reaction mixture was kept cool in dry-ice bath at -70 °C. After the addition of COF₂ was complete, the reaction mixture was allowed to warm up to room temperature. The methyl fluoroformate was distilled and recovered. Purity by ¹⁹F-NMR and ¹H-NMR: >99.5% molar.

3.3. Typical procedure for the alkylation reaction

3.3.1. Reactions at temperatures between 25 and 75 $^{\circ}C$

An amount of 21 mmol of cesium fluoride (dried at 320 °C under high vacuum for 3 h), 14 g of solvent (tetraglyme or one of the other solvents reported in Table 1), 10.5 mmol of DAF (MW = 474, Bp = 112–114 °C) and 50 mmol of methyl fluoroformate were charged in a 50 ml three necked glass flask equipped with a condenser, a stirring bar and two rubber septa. The mixture was kept under stirring at room temperature for 30 min and then warmed up to the reaction temperature. All the reactions were stopped at degree of conversion lower than 50% so that the variation of concentration of methyl fluoroformate could be considered approximately constant. For the calculation of k_2 we assumed that [CH₃OCOF] during the reaction was equal to its initial value [CH₃OCOF]₀.

Periodic samples of about 1 ml were taken by using a syringe and analysed via ¹⁹F-NMR.

3.3.2. Reaction at 110 °*C*

An amount of 21 mmol of metal fluoride (dried at 320 °C under high vacuum for 3 h), 14 g of tetraglyme and 10.5 mmol of DAF (MW = 474, Bp = 112–114 °C) were charged in a 50 ml three necked glass flask, a stirring bar and two rubber septa. The mixture was kept under stirring at room temperature for 30 min and then warmed up to 110 °C. At this temperature methyl fluoroformate was fed into the mixture (80 mmol h⁻¹). Periodic samples of about 1 ml were taken and analysed via ¹⁹F-NMR. The concentration of methyl fluoroformate was found to be constant during all the reaction (0.3 mol l⁻¹).

3.3.3. Reaction at 150 $^{\circ}C$

The procedure is the same reported in Section 3.3.2 but a higher boiling point fraction of DAF was used (MW = 824, Bp > 190 °C) to avoid the evaporation of this reactant. Periodic samples of about 1 ml were taken to determine the concentration of methyl fluoroformate (which was constant and equal to 0.2 mol l^{-1}) and of the other reagents.

3.3.4. Reaction with triethylamine hydrofluoride (*Et*₃*N*·*HF*)

An amount of 7 mmol of triethylamine trihydrofluoride was charged in a 50 ml three necked glass flask equipped with a condenser, a stirring bar and two rubber septa. After cooling the system at 0 °C with an ice bath, 14 mmol of triethylamine were slowly added in the flask. After the addition was complete, the reaction mixture was allowed to warm slowly to room temperature and 14 g of tetraglyme, 10.5 mmol of DAF (MW = 474, Bp = 112–114 °C) and 50 mmol of methyl fluoroformate were added. The mixture was kept under stirring at room temperature for 30 min and then warmed up to 50 °C. Periodical samples of about 1 ml were taken and analysed.

3.4. ¹⁹F-NMR analysis

¹⁹F-NMR spectra were recorded on Variant Mercury 200 MHz spectrometer using CFCl₃ as internal standard.

4. Conclusion

DM-FPEs were obtained by alkylation of DAF with methyl fluoroformate in the presence of a fluoride anion source in solvent. Several conditions were tested; among them are type of solvent, temperature, type and amount of the fluoride source. The best results were obtained using tetraglyme as solvent and CsF as fluoride metal source.

The estimated rate constant k_2 using CsF in tetraglyme ranges between $10^{-7} 1 \text{ mol}^{-1} \text{ s}^{-1}$ at 30 °C and $10^{-3} 1 \text{ mol}^{-1} \text{ s}^{-1}$ at 150 °C. The Arrhenius plot well fits the experimental data, yielding an activation energy of 17 kcal mol⁻¹. Good results were also obtained with tetraglyme and KF, being the reaction rate at 50 °C comparable with that obtained with CsF, whereas at 110 °C a slight difference was observed. For the industrial practice, KF might be more advantageous for its lower commercial cost compared to CsF and for the possibility to regenerate the deactivated form (KHF₂) by thermal treatment.

Acknowledgements

The authors wish to thank Renzo Bartolini for the syntheses, the Analytical and Material Science Department for the analytical characterizations and Solvay Solexis for permission to publish this work.

References

- [1] G. Marchionni, M. Visca, Eur. Pat. Appl. 1275678A (2003).
- [2] M.P. Sulbaek Andersen, M.D. Hurley, T.J. Wallington, F. Blandini, N.R. Jensen, V. Librando, J. Hjorth, G. Marchionni, M. Avataneo, M. Visca, F.M. Nicolaisen, O.J. Nielsen, J. Phys. Chem. A 108 (2004) 1964–1972.
- [3] G. Marchionni, S. Petricci, P.A. Guarda, G. Spataro, G. Pezzin, J. Fluorine Chem. 125 (2004) 1081–1086.
- [4] G. Marchionni, P. Maccone, G. Pezzin, J. Fluorine Chem. 118 (2002) 149–155.
- [5] G. Marchionni, M. Avataneo, U. De Patto, P. Maccone, G. Pezzin, J. Fluorine Chem., in press.
- [6] G. Marchionni, U. De Patto, M. Avataneo, Eur. Pat. Appl. 1346757 (2003).
- [7] J.L. Adcock, R.A. Beh, R.J. Lagow, J. Org. Chem. 40 (1975) 3271– 3275.
- [8] R.D. Chambers, B. Grievson, J. Fluorine Chem. 29 (1985) 323-339.
- [9] S. Modena, P. Calini, G. Gregorio, G. Moggi, J. Fluorine Chem. 40 (1988) 349–357.
- [10] R.D. Chambers, A.K. Joel, A.J. Rees, J. Fluorine Chem. 101 (2000) 97–105.
- [11] A.L. Henne, M.A. Smook, J. Am. Chem. Soc. 72 (1950) 4378-4380.
- [12] M.G. Costello, US Patent 5741950 (1998).
- [13] D.R. Vitcak, M.R. Flynn, US Patent 5750797 (1998).

- [14] F.E. Behr, Y. Cheburkov, US Patent 6023002 (2000).
- [15] W.M. Lamanna, R.M. Flynn, D.R. Vitcak, Z.M. Qiu, US Patent 6046368 (2000).
- [16] W. Navarrini, M. Galimberti, G. Fontana, US Patent 0192974 (2004).
- [17] Williams, et al. Trans. Faraday Soc. 67 (1971) 922–928.
- [18] T. Suyama, S. Kato, J. Fluorine Chem. 56 (1992) 93-99.
- [19] Bock, et al. Can. J. Chem. 46 (1968) 1645-1648.
- [20] C.W. Tullock, D.D. Coffman, J. Org. Chem. 25 (1960) 2016–2019.
- [21] F.W. Evans, M.H. Litt, A.-M. Weidler-Kubanek, F.P. Avonda, J. Org. Chem. 33 (1968) 1837–1839.
- [22] G. Marchionni, M. Visca, US Patent 0013923 (2003).
- [23] J. Murata, M. Tamura, A. Sekiya, J. Fluorine Chem. 113 (2002) 97– 100.
- [24] H. Zhang, D. Dearden, J. Am. Chem. Soc. 114 (1992) 2754-2755.
- [25] R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, D. Sen, Chem. Rev. 85 (1985) 271–339.
- [26] Y. Cheburkov, G.J. Lillquist, J. Fluorine Chem. 118 (2002) 123-126.
- [27] D. Sianesi, G. Marchionni, R.J. De Pasquale, in: R.E. Banks (Ed.), Organofluorine Chemistry: Principles and Commercial Applications, Plenum Press, New York, 1994.
- [28] G. Marchionni, G. Ajroldi, G. Pezzin, in: S.L. Aggarwal, S. Russo (Eds.), Comprehensive Polymer Science, Second Supplement, Pergamon Press, London, 1996.
- [29] G. Marchionni, P.A. Guarda, US Patent 5744651 (1998).
- [30] D. Sianesi, G. Caporiccio, US Patent 3847978 (1974).