

## A study of the thermal decarboxylation of three perfluoropolyether salts

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### Abstract

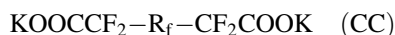
The thermal decarboxylation of three dicarboxylic perfluoropolyether potassium salts of relatively short chain length has been investigated and the products and kinetics of the main reactions have been defined. From the rate constants and Arrhenius parameters data, the second decarboxylation appears to be quantitatively rather close to the first.

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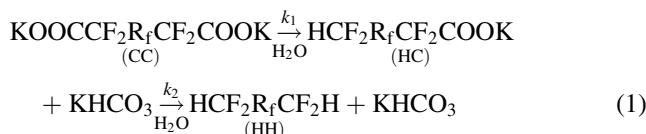
*Keywords:*  $\alpha,\omega$ -Dihydroperfluoropolyethers; Perfluoropolyether potassium salts; Thermal decarboxylation; Kinetic parameters

### 1. Introduction

The thermal decarboxylation of perfluoropolyether potassium dicarboxylic salts having the structure:

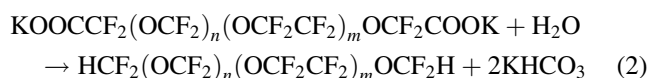


where  $\text{R}_f$  is a short moiety, when carried out in the presence of an excess of a proton donor, such as water, proceeds through a decarboxylation reaction that leads to the monocarboxylate compound (HC), and a second reaction that gives the final  $\alpha,\omega$ -hydrogenated product (HH). Schematically:



In the present paper, the kinetics and the mechanisms of the thermal decarboxylations of three perfluoropolyether potassium salts of relatively high purity (>95% molar) are described, their formulae are:  $\text{KOCCF}_2\text{OCF}_2\text{COOK}$  ( $\text{R}_f = \text{-O-}$ ) CC1,  $\text{KOCCF}_2\text{OCF}_2\text{OCF}_2\text{COOK}$  ( $\text{R}_f = \text{-OCF}_2\text{O-}$ ) CC2 and  $\text{KOCCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{COOK}$  ( $\text{R}_f = \text{-OCF}_2\text{CF}_2\text{O-}$ ) CC3.

They are models for more complex salts of higher molecular weight (e.g. the H-Galden<sup>®</sup> ZT) [1–4], whose reactions are:



Here  $n$  and  $m$  are either zero or integers. The aim of the present work is to study the kinetics of the main thermal reactions, to obtain relevant kinetic parameters, and to clarify the reactions mechanisms. The literature on similar reactions appears to be relatively scarce [5–10].

### 2. Results and discussion

#### 2.1. Decarboxylation of $\text{KOCCF}_2\text{OCF}_2\text{COOK}$ (CC1)

The thermal reactions of CC1 have been investigated at four temperatures: 140, 160, 180 and 200 °C, by determining the chemical composition of both the liquid and gaseous phases present in the reaction vessel at a number of selected times (for clarity, the analytical data reported in the present paper, refer to only one time for each temperature). The most significant results are the final degree of conversion at the time selected, (with respect to the initial quantity of dicarboxylic salt CC1), and the quantity of  $\alpha,\omega$ -hydrogenated product (HH1), both results being expressed as mol% (Table 1). Percentage errors ( $E\%$ ) relative to the material balance of the carbon and fluorine content, calculated with

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Table 1

Degree of conversion of the dicarboxylic salt  $\text{KOOCCF}_2\text{OCF}_2\text{COOK}$  (CC1), yield of  $\text{HCF}_2\text{OCF}_2\text{H}$  (HH1), and material balance of carbon and fluorine at the temperature and time indicated

Run	$T$ ( $^{\circ}\text{C}$ )	Time (min)	CC1 conversion (%)	HH1 yield (%)	Carbon (E%)	Fluorine (E%)
1	140	2900	85.0	7.70	-3.3	-3.2
2	160	1450	99.8	34.7	-6.1	-7.3
3	180	70	87.2	21.6	-2.7	-2.7
4	200	20	94.9	38.9	-5.8	-4.5

Table 2

Analytical data, expressed as concentration of the species ( $\text{mol l}^{-1}$ ), recovered after decarboxylation reactions

Run	CC1	HC1	HH1	CC2	HC2	HH2	CC3	HC3	HH3	(COOK) <sub>2</sub>	HCOOK	F <sup>-</sup>	CHF <sub>3</sub>	CO	CO <sub>2</sub>
4	0.017	0.062	0.129	-	-	-	-	-	-	0.017	0.047	0.374	-	0.124	0.252
9	-	-	-	0.001	0.004	0.170	-	-	-	0.010	0.080	0.389	0.030	0.004	0.454
13	0.020	0.026	0.006	-	-	-	0.001	0.003	0.148	0.002	0.044	0.203	0.018	0.007	0.277

The initial amounts of the three bicarboxylic salts are respectively: CC1  $0.332 \text{ mol l}^{-1}$ ; CC2  $0.266 \text{ mol l}^{-1}$  and CC3  $0.249 \text{ mol l}^{-1}$ .

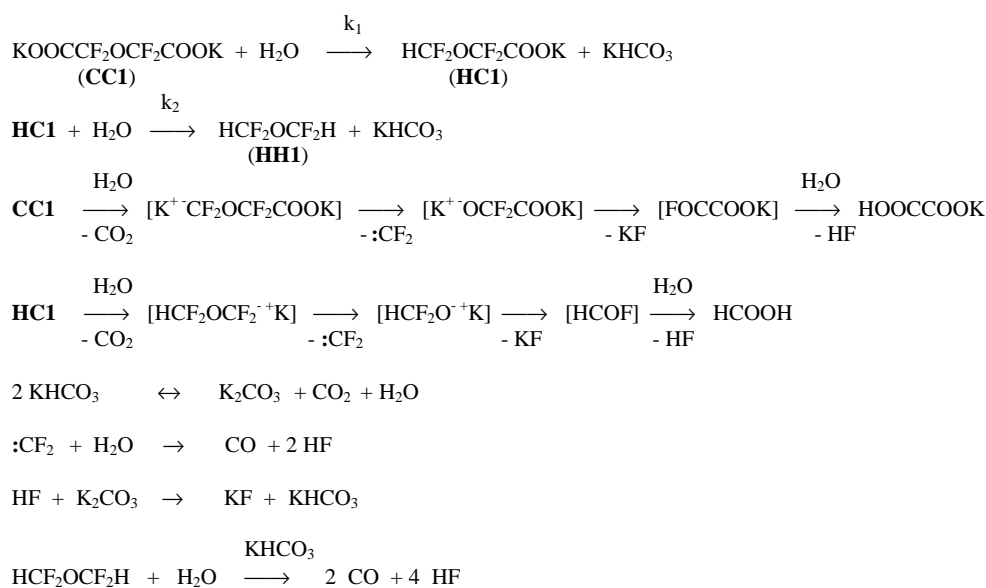
respect to the stoichiometry of the processes, are also reported, in Table 1. As an example, the concentrations of all the species recovered after the decarboxylation reaction relevant to run 4 are collected in Table 2.

The errors in the carbon and fluorine material balance remain almost constant (and relatively small) with increasing decarboxylation temperature, a result that can be interpreted as an indication that the material balance is substantially correct. At the times selected for the tests, an increase of temperature leads to an increase of both the final degree of conversion of CC1 and of yield of HH1, the latter reaching moderately high values at temperatures in the range 160–200  $^{\circ}\text{C}$ , the selected reaction time being as low as 20 min at the highest temperature explored. All the possible salt decarboxylation reactions are given in Scheme 1, in which the analytical results are summarized.

The anionic intermediates  $\text{CF}_2\text{OCF}_2\text{COOK}$  and  $\text{CF}_2\text{OCF}_2\text{H}$  are present in these reactions, in which degradation of intermediate products also plays a role, as demonstrated by the presence of potassium oxalates and formates (the latter however has been experimentally monitored only at 200  $^{\circ}\text{C}$ ).  $\text{CHF}_3$  is absent in the reaction products; even a decarboxylation reaction carried out at 200  $^{\circ}\text{C}$  in the presence of excess fluoride ions (KF) did not result in the production of  $\text{CHF}_3$ .

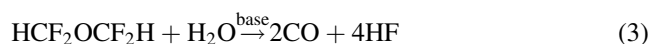
From Table 1 it appears that the  $\alpha,\omega$ -hydrogenated products yields are not very high, even when the reaction proceeds to high degrees of conversion, and that only when the temperature is high are the  $\alpha,\omega$ -hydrogenated products relatively abundant.

The above results lead to the tentative conclusion that in a basic medium  $\text{HCF}_2\text{OCF}_2\text{H}$  undergoes degradation



Scheme 1. Reaction mechanism for the thermal decarboxylation of salt CC1.

to CO and HF:



a reaction apparently related to the acidity of the hydrogen atoms of the HH1 product.

To verify the above hypothesis, the thermal stability of the HH1 molecule has been tested separately under reaction conditions. In particular, when 5 ml (0.22 mol) of  $\text{HCF}_2\text{OCF}_2\text{H}$  were heated at 160 °C for 5 h with 0.5% aqueous basic solutions of  $\text{KHCO}_3$ , fluorides were formed in the aqueous phase and CO and  $\text{CO}_2$  in the gas phase, 50% of the reagent  $\text{HCF}_2\text{OCF}_2\text{H}$  being consumed.

Under neutral conditions the reagent HH1 is stable, as shown by the fact that after treatment for 20 min at 200 °C in the presence of a 10% (w/w) KF solution, it is completely recovered.

The low yields of  $\alpha,\omega$ -hydrogenated products suggest that the reactions are rather complex. To obtain kinetic parameters a simplified reaction scheme cannot be used and only the kinetic constant of the CC1 consumption can be obtained as a function of temperature.

The reaction appears to be first order from Fig. 1, where the CC1 concentration is plotted on a log scale against time. The linear relationships between  $k_s$  at each temperature, reported in Table 3, and  $1/T$  (Figure not shown), give the Arrhenius parameters of the reaction as  $E_a = 3$  (kcal mol<sup>-1</sup>) and  $A = 3.6 \times 10^{12}$  s<sup>-1</sup>.

## 2.2. Decarboxylation of $\text{KOOCCF}_2\text{OCF}_2\text{OCF}_2\text{COOK}$ (CC2)

The reactions have been carried out at 140, 150, 160, 170 and 180 °C, the compositions being monitored, at selected

Table 3

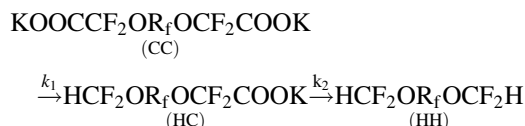
The kinetic constant of degradation of salt  $\text{KOOCCF}_2\text{OCF}_2\text{COOK}$  (CC1) at different temperature

Temperature (°C)	$k_s$ (s <sup>-1</sup> )
140	$1.1 \times 10^{-5}$
160	$7.2 \times 10^{-5}$
180	$5.1 \times 10^{-4}$
200	$2.2 \times 10^{-3}$

times, in both the aqueous and gas phases. The final amounts of reagent and products are summarized in Table 4 and the reaction mechanisms are reported in Scheme 2. As example, the concentrations of all the species recovered after decarboxylation reaction relevant to run 9, are collected in Table 2. When the conversion of the dicarboxylic salt is high, the yield of the  $\alpha,\omega$ -hydrogenated product is also high, and the concentrations of oxalate, formate, CO and  $\text{CHF}_3$ , produced by parallel reactions are small.

In the limit of zero production of the latter compounds, i.e. when parallel reactions are absent, the data can be treated using a simplified kinetic model of consecutive first-order reactions, which allows evaluation of the kinetic constants at various temperatures.

For the general reactions:



the following kinetic equations can therefore be applied:

$$\frac{d[\text{CC}]}{dt} = -k_1[\text{CC}] \quad (4)$$

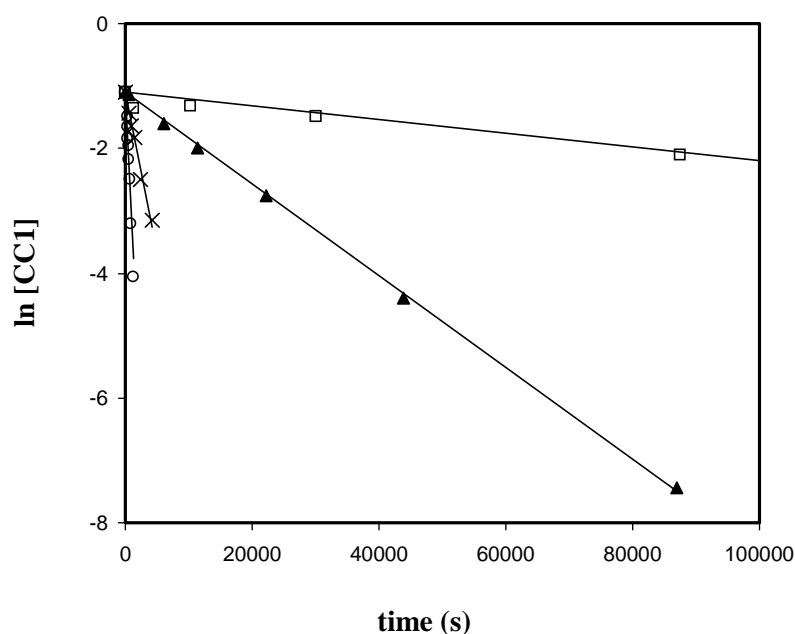


Fig. 1.  $\text{KOOCCF}_2\text{OCF}_2\text{COOK}$  (CC1) salt concentration vs. time at 140 °C ( $\square$ ), 160 °C ( $\blacktriangle$ ), 180 °C ( $\times$ ) and 200 °C ( $\circ$ ).

Table 4

Degree of conversion of the dicarboxylic salt KOCCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>COOK (CC2), yield of HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>H (HH2), and material balance of carbon and fluorine

Run	<i>T</i> (°C)	Time (min)	CC2 conversion (%)	HH2 yield (%)	Carbon ( <i>E</i> %)	Fluorine ( <i>E</i> %)
5	140	980	99.0	65.3	−7.2	−5.9
6	150	160	91.7	59.2	−3.5	−4.8
7	160	130	98.9	67.3	−3.0	−3.3
8	170	60	99.8	67.4	−6.8	−4.8
9	180	40	99.5	63.7	−7.0	−2.1

$$\frac{d[\text{HC}]}{dt} = k_1[\text{CC}] - k_2[\text{HC}] \quad (5)$$

$$\frac{d[\text{HH}]}{dt} = k_2[\text{HC}] \quad (6)$$

The concentration of CC follows a first-order decay equation:

$$[\text{CC}] = [\text{CC}]_0 e^{-k_1 t} \quad (7)$$

(where  $[\text{CC}]_0$  is the initial CC concentration).

When, at time zero, the concentration of HC and HH is zero, the differential equation becomes:

$$\frac{d[\text{HC}]}{dt} = k_1[\text{CC}]_0(e^{-k_1 t}) - k_2[\text{HC}] \quad (8)$$

and therefore:

$$[\text{HC}] = \frac{k_1[\text{CC}]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (9)$$

From the material balance one obtains, in the absence of parallel reactions:

$$[\text{HH}] = [\text{CC}]_0 \left( 1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right) \quad (10)$$

Table 5

Constant of first and second decarboxylation reaction of salt KOCCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>COOK (CC2) at various temperatures

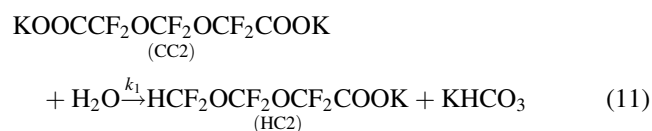
Temperature (°C)	<i>k</i> <sub>1</sub> (s <sup>−1</sup> )	<i>k</i> <sub>2</sub> (s <sup>−1</sup> )
140	$7.5 \times 10^{-5}$	$1.0 \times 10^{-4}$
150	$2.5 \times 10^{-4}$	$5.1 \times 10^{-4}$
160	$8.5 \times 10^{-4}$	$1.3 \times 10^{-3}$
170	$1.9 \times 10^{-3}$	$1.9 \times 10^{-3}$
180	$5.9 \times 10^{-3}$	$5.7 \times 10^{-3}$

By applying Eq. (7) to the experimental data the first decarboxylation reaction constant  $k_1$  is obtained. Successively a procedure is applied that optimizes the  $k_2$  value by minimizing the sum of the quadratic differences between the HC2 and HH2 values obtained from Eqs. (9) and (10) and the experimental values. The results are collected in Table 5.

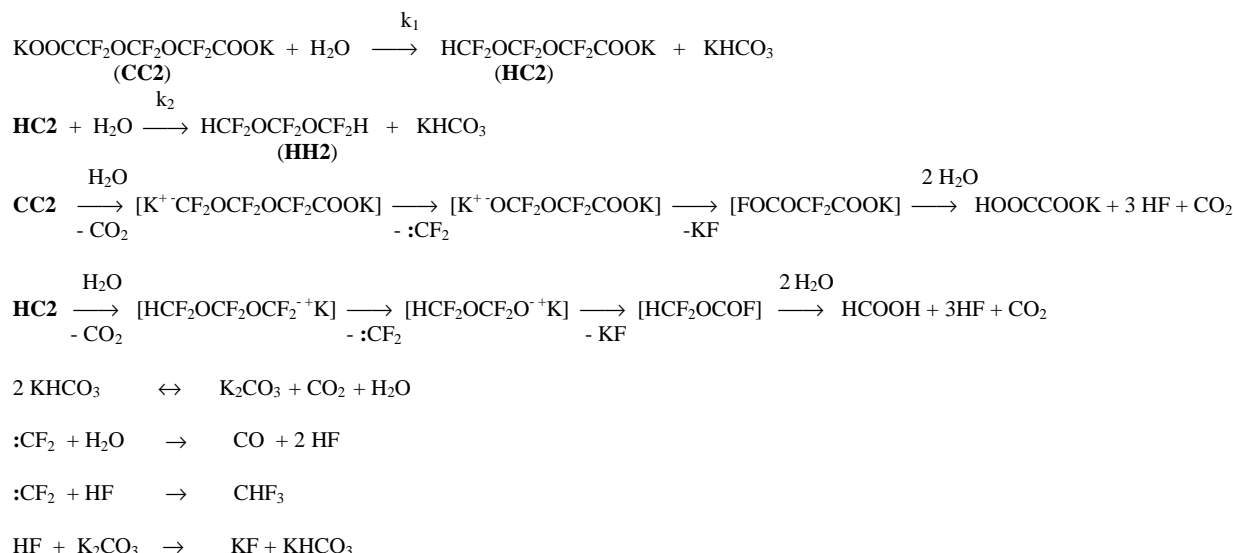
The experimental CC2, HC2 and HH2 concentrations, plotted as a function of time, and those calculated, derived from Eqs. (7), (9) and (10), in which the optimized values of the  $k_1$  and  $k_2$  are inserted, compare satisfactorily for the CC2 and HC2 values, but not for HH2: this result is due to the fact that the simplified model used does not take into account parallel degradation reactions. As example, in Fig. 2 calculated and experimental kinetic data relatively to run 7 are reported.

From a suitable plot, (Fig. 3) the Arrhenius parameters  $E_a$  and  $A$  have been obtained.

For the first decarboxylation reaction:



$$E_a(1) = 40 \text{ (kcal mol}^{-1}\text{)}; A(1) = 1.1 \times 10^{17} \text{ s}^{-1}.$$



Scheme 2. Reaction mechanism for the thermal decarboxylation of salt CC2.

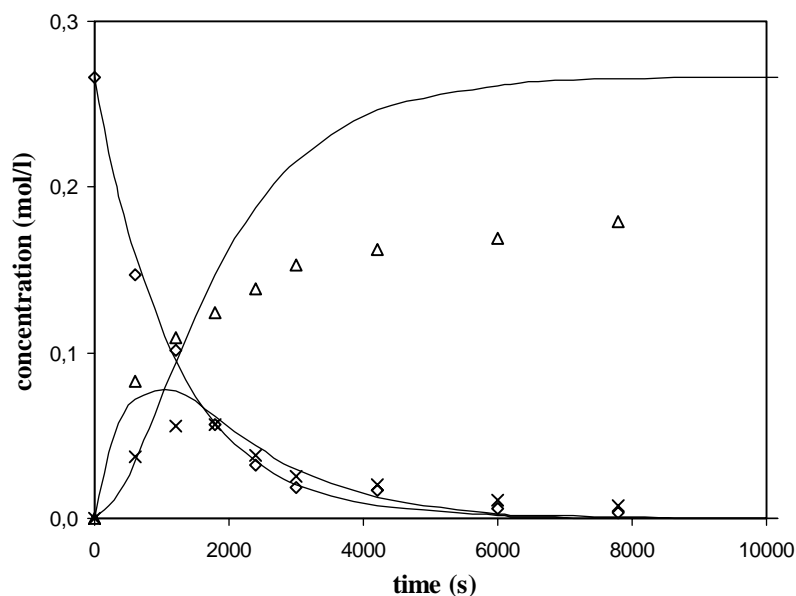


Fig. 2. Decarboxylation of CC2 salt at 160 °C (run 7): experimental data relating to CC2 ( $\diamond$ ), HC2 ( $\times$ ) and HH2 ( $\triangle$ ) species, in comparison with calculated trends (continuous lines). See text for discussion of the above data.

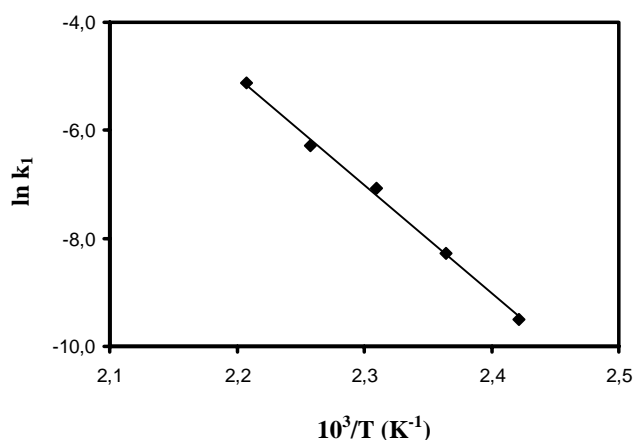
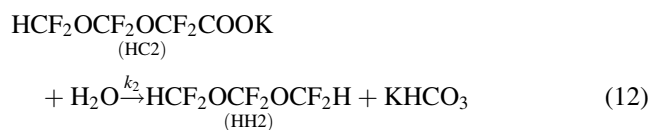


Fig. 3. Arrhenius plot of kinetic constant  $k_1$  for the thermal decarboxylation of salt CC2.

For the second decarboxylation reaction:



$$E_a(2) = 35 \text{ (kcal mol}^{-1}\text{)}; A(2) = 3.8 \times 10^{14} \text{ s}^{-1}.$$

### 2.3. Decarboxylation of $\text{KOCCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{COOK}$ (CC3)

The reactions have been carried out at 140, 150, 160 and 170 °C, the compositions being monitored, at selected time intervals, in both the aqueous and gas phases.

In Table 6, the relevant data are collected, for each temperature, as well as the material balance of carbon and fluorine, expressed as percentage errors  $E\%$ . As an example, the concentrations of all the species recovered after decarboxylation reaction relevant to run 13, are collected in Table 2.

The material balances of fluorine and carbon are affected by errors larger than those of CC1 and CC2. In the temperature range explored, the  $\alpha,\omega$ -hydrogenated products yields are close to 60%. The reaction mechanisms are shown in Scheme 3; it is interesting to point out the presence of the CC1, HC1 and HH1 species, whose formation has been described.

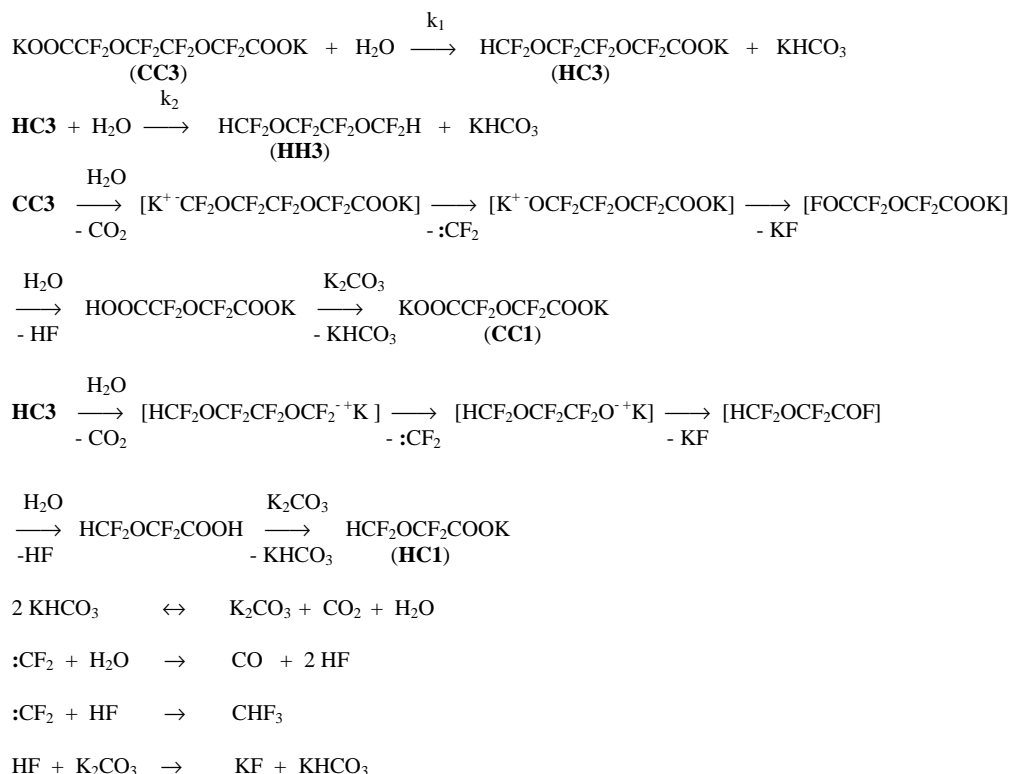
When the simplified kinetic model of consecutive reactions is applied to these data, using Eqs. (7), (9) and (10), and the results are optimized as described previously, one obtains the kinetic constants collected in Table 7.

As already reported for CC2, the experimental CC3, HC3 and HH3 concentrations, plotted as a function of time, and

Table 6

Degree of conversion of the dicarboxylic salt  $\text{KOCCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{COOK}$  (CC3), yield of  $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$  (HH3), and material balance of carbon and fluorine

Run	$T$ (°C)	Time (min)	CC3 conversion (%)	HH3 yield (%)	Carbon ( $E\%$ )	Fluorine ( $E\%$ )
10	140	500	98.0	55.7	-6.9	-7.5
11	150	120	95.6	52.7	-4.7	-6.1
12	160	100	99.8	60.4	-15.1	-11.0
13	170	40	99.7	59.6	-9.4	-11.8



Scheme 3. Reaction mechanism for the thermal decarboxylation of salt CC3.

Table 7  
Constant of first and second decarboxylation reaction of  $\text{KOOCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{COOK}$  (CC3) at various temperatures

Temperature ( $^{\circ}\text{C}$ )	$k_1$ ( $\text{s}^{-1}$ )	$k_2$ ( $\text{s}^{-1}$ )
140	$1.3 \times 10^{-4}$	$1.0 \times 10^{-4}$
150	$4.3 \times 10^{-4}$	$3.6 \times 10^{-4}$
160	$1.1 \times 10^{-3}$	$9.5 \times 10^{-4}$
170	$3.1 \times 10^{-3}$	$1.8 \times 10^{-3}$

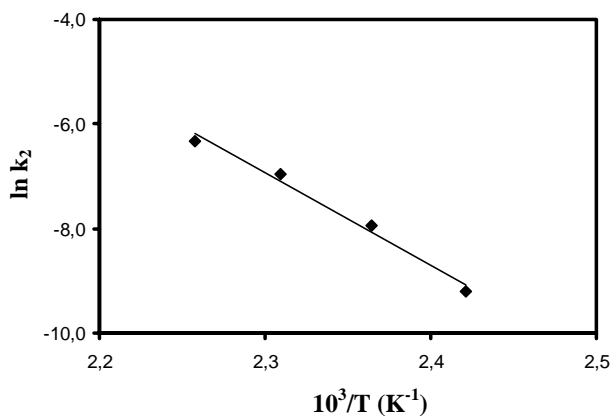
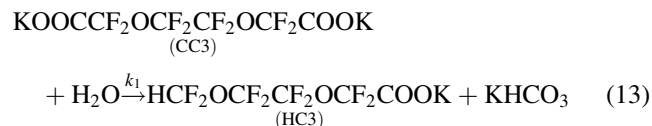


Fig. 4. Arrhenius plot of kinetic constant  $k_2$  for the thermal decarboxylation of salt CC3.

those calculated, derived from Eqs. (7), (9) and (10) (in which the optimized values of the  $k_1$  and  $k_2$  are inserted), compare satisfactorily for CC3 and HC3, but not for HH3, a result which is due to the fact that the simplified model used does not take into account parallel degradation reactions.

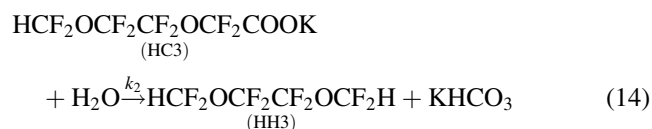
From an appropriate plot of the above data (Fig. 4), the Arrhenius parameters  $E_a$  and  $A$  have been obtained.

For the first decarboxylation reaction:



$$E_a(1) = 38 \text{ (kcal mol}^{-1}\text{)}; A(1) = 2.1 \times 10^{16} \text{ s}^{-1}.$$

For the second decarboxylation reaction:



$$E_a(2) = 35 \text{ (kcal mol}^{-1}\text{)}; A(2) = 4.7 \times 10^{14} \text{ s}^{-1}.$$

### 3. Conclusions

The present paper summarizes the main features of the thermal decarboxylation reactions of representative dicarboxylic potassium salts having rather short perfluorinated

chains, that represent a simplified model of longer species, precursor in the production of the H-Galden<sup>®</sup> ZT compounds. Mechanisms are proposed for the principal two-step ionic decarboxylations, as well as for some secondary degradation processes taking place.

A parallel process has been found to give, in the CC2 and CC3 reactions, the intermediate species difluorocarbene :CF<sub>2</sub>, together with oxalate and formate and the short chain CC1 compound, respectively. The overall reactions leading to the final  $\alpha,\omega$ -hydrogenated products are characterized, for the CC2 and CC3 salts, by yields close to 60–65%, which do not appear to be very temperature dependent in the range explored.

A peculiar consecutive reaction characterizes the degradation of the short chain CC1 salt; the expected decarboxylation product HH1 is unstable under the reaction conditions and degrades further to CO and fluorides.

For the CC1 compounds the temperature dependence of the kinetic constant has been obtained for the salt consumption. For the CC2 and CC3 salts the kinetic model of first-order consecutive reactions was used, from which both the kinetic constants of the first and the second decarboxylation as well as the relative Arrhenius parameters have been derived. Small differences in the reaction rates are present, at a given temperature, for CC2 and CC3; moreover, the kinetic constants of the first and second decarboxylation are rather close, particularly for the CC3 compound. Even when two carboxylic groups are as close as in the short molecules investigated here, there is little mutual influence, and therefore any influence will presumably be absent in compounds having longer chains.

## 4. Experimental

### 4.1. Preparation of dicarboxylic potassium salts

The  $\alpha,\omega$ -diethyl esters CH<sub>3</sub>CH<sub>2</sub>OOCF<sub>2</sub>-R<sub>f</sub>-CF<sub>2</sub>COO-CH<sub>2</sub>CH<sub>3</sub> were obtained from oxidative polymerization of tetrafluoroethylene with oxygen using UV irradiation, followed by catalytic reduction and successive esterification

Table 8  
Quantitative analysis of dicarboxylic potassium salts

Product	MW	Molar (%)
KOCCF <sub>2</sub> OCF <sub>2</sub> COOK (CC1)	282	99.0
KOCCF <sub>2</sub> OCF <sub>2</sub> OCF <sub>2</sub> COOK (CC2)	348	96.3
KOCCF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub> OCF <sub>2</sub> COOK (CC3)	398	99.4

with ethanol. Details of the processes are described elsewhere [11]. Pure salts have been prepared from a selective fractionation of diethyl esters followed by an aqueous hydrolysis with quantitative amounts of KOH, a suitable distillation of the ethanol–water azeotrope, and a final dehydration in an oven at 90 °C. In Table 8, molecular weight and quantitative analysis of the dicarboxylic salts are reported. In order to determinate the purity of the above compounds, <sup>19</sup>F NMR quantitative analysis on aqueous solutions containing 10% by weight of salt, were performed.

### 4.2. Experimental apparatus of thermal decarboxylation

Due to the impossibility of extracting directly, at selected times, successive portions of the reaction mixture from the decarboxylation vessel, in order to follow the reaction kinetics, suitable parallel batch experiments were carried out on 10 g solutions, each containing 10% by weight of salt, and the relative aqueous and gas phases were analysed. For each decarboxylation test 10 steel AISI 316 cylindrical 20 ml flask were used. They were thermostatted in a bath oil at the selected temperature. Rapid immersion, the extraction and the forced cooling of the steel vessels was provided by a suitable mechanical apparatus.

### 4.3. Analytical section

In order to extract completely the gaseous products in the vapor phase, the decarboxylation vessels were heated at 50 °C and then connected to a volumetric flask under vacuum. The gas phases were then analysed by gas chromatography using a gas chromatograph, type CE 8000 Top

Table 9  
Chemical shifts and coupling constants for <sup>19</sup>F NMR signals of carboxylic salts

Product	Chemical shift (ppm) <sup>a</sup>				Coupling const. (Hz)			
	1	2	3	4	1–2	2–3	3–4	F–H
KOCCF <sub>2</sub> <sup>1</sup> OCF <sub>2</sub> COOK (CC1)	–78.0 (s)							
KOCCF <sub>2</sub> <sup>1</sup> OCF <sub>2</sub> <sup>2</sup> H (HC1)	–78.9 (t)	–85.4 (dt)			4.9			69.7
KOCCF <sub>2</sub> <sup>1</sup> OCF <sub>2</sub> <sup>2</sup> OCF <sub>2</sub> COOK (CC2)	–52.2 (quint)	–79.9 (t)			9.8			
KOCCF <sub>2</sub> <sup>1</sup> OCF <sub>2</sub> <sup>2</sup> OCF <sub>2</sub> <sup>3</sup> H (HC2)	–79.9 (t)	–54.3 (tt)	–86.9 (dt)		9.8	4.9		69.7
KOCCF <sub>2</sub> <sup>1</sup> OCF <sub>2</sub> <sup>2</sup> CF <sub>2</sub> OCF <sub>2</sub> COOK (CC3)	–78.4 (t)	–89.4 (t)			11.4			
KOCCF <sub>2</sub> <sup>1</sup> OCF <sub>2</sub> <sup>2</sup> CF <sub>2</sub> <sup>3</sup> OCF <sub>2</sub> <sup>4</sup> H (HC3)	–78.5 (t)	–89.3 (t)	–89.9 (t)	–86.0 (dt)	11.4		4.9	69.7

<sup>a</sup> With reference to CFCl<sub>3</sub>.

with TCD detector. In order to analyse the hydroderivates HH1, HH2 and HH3 a copper packed column was used (diameter 4 mm, length 2 m) filled with Fomblin<sup>®</sup> M10 in ratio 20/100 on Chromosorb P 60–80 mesh. In the analysis for CO<sub>2</sub>, CO and CHF<sub>3</sub> a steel packed column was used (diameter 1/8 in., length 3 m), filled with 100/120 Carbo-sieve S-II (Supelco). Quantitative analysis were performed using suitable gas chromatographic response factors, previously determined analyzing the pure compounds.

Ion chromatography was used for the analysis of oxalates, formates, fluorides and mono- and dicarboxylic fluorinated compounds in the aqueous phases. All solutions, diluted by a factor of about 100, were analysed using a IONPAC AS11 column with a gradient of NaOH (from 5 to 100 mM). In the analysis of fluorides, oxalates, formates and dicarboxylic salts, the calibration was performed using aqueous solutions containing known amounts of pure compounds; decarboxylated solutions previously analysed by <sup>19</sup>F NMR were used in order to determine the amounts of monocarboxylic salts.

<sup>19</sup>F NMR spectroscopy was used for quantitative analysis of carboxylic salts: the spectra of the aqueous solutions were recorded using a Varian Inova 400 spectrometer, at 376 MHz. The quantitative analysis were performed using an internal capillary tube containing a known amount of a fluorinated standard. In Table 9, all chemical shifts and coupling constants for the mono- and dicarboxylic salts examined are collected.

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