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1. Introduction

Perfluorodiacyl peroxides are an interesting and useful source of perfluoroalkyl radicals.

Their utility as initiators in free radical polymerizations has been recognized since the early fifties even though many studies have been done in hydrogenated free radical chemistry. Recently perfluoroalkyl free radical chemistry has obtained a considerable interest and many articles have appeared in the specialized literature.

Among the initiation processes, the thermal decomposition of perfluorodiacyl peroxides is a very convenient method for solution and bulk polymerizations of fluoro-monomers.

This is mainly due to very clean reactions and mild thermal conditions to generate perfluoroalkyl radicals and, in the range of peroxide concentration used in the polymerization, the auto-induced decomposition of perfluoroalkyl peroxides is not observed. Secondly, this initiation system cannot act as a free radical transfer reagent, giving a better control of the molecular weights of the polymers. Moreover, perfluoroalkyl radicals are directly introduced as terminal groups allowing the preparation of fluoropolymers with excellent thermal and optical properties and avoiding a secondary fluorination treatment to stabilize the obtained polymers.

The presence of electron withdrawing groups like fluorine or perfluoroalkyl radicals bonded to the carbonyl of the acylperoxide also enhances their thermal homolytic decomposition rate as it has been observed by Swada<sup>[1]</sup>. In fact fluorocarbonyl peroxides decompose more rapidly as compared to the hydrogenated peroxides.

We addressed our study toward the preparation of a class of perfluorodiacyl peroxide characterized by decomposition temperatures ranging from 0°C up to 90°C, with a half-life time of few hours in order to utilize them as initiators in broad polymerization reaction conditions.

2. Synthesis

2.1. Perfluorinated acyl fluorides

Perfluorinated diacyl peroxides (as well as hydrogenated diacyl peroxides) can be prepared by the reaction between acyl halides (usually chlorides or fluorides) or anhydrides and an aqueous solution of NaOH and H<sub>2</sub>O<sub>2</sub>. The yields are better with acyl chlorides and anhydrides, unfortunately these compounds are less available than perfluoroalkyl fluorides.

The availability of the starting reagents oriented our choice towards the perfluorinated acyl fluorides, obtained by condensation between carbonyl fluoride and perfluoroolefins in presence of suitable catalysts (like fluorides of cesium and potassium). This reaction (reported in the literature since the sixties) has been studied both in continuous systems and in batch systems, reaching conditions which lead to good productivity towards the wished acyl fluoride. In the following table the utilized perfluoroolefins are reported as well as the corresponding acyl fluoride and operating conditions.

Olefin	Acyl fluoride	COF <sub>2</sub> /olef. ratio	Temp. (°C)	Catalyst	Yield
c-C <sub>4</sub> F <sub>8</sub> (1)	c-C <sub>4</sub> F <sub>7</sub> -COF	1,5	100°C	CsF/THG	91%
CF <sub>3</sub> CF=CF <sub>2</sub> (2)	(CF <sub>3</sub> ) <sub>2</sub> CFCOF	1,15	190°C	Supp. CsF	95%
CF <sub>3</sub> CF=CF <sub>2</sub> (3)	(CF <sub>3</sub> )CF <sub>2</sub> OFCOF	1,6	210°C	Supp. CsF	93%
(CF <sub>3</sub> O) <sub>2</sub> C=CF <sub>2</sub> (4)	(CF <sub>3</sub> O) <sub>2</sub> CF <sub>2</sub> OFCOF	1,25	200°C	Supp. CsF	60%

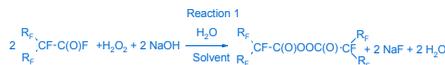
The synthesis have been carried out both in a flow system (2,3) and in batch (1,4). When the starting material was an  $\alpha$  olefin, it was used as catalyst solid CsF (opportunistly supported on an inert material to increase the active surface), while using the perfluorocyclobutane it was necessary to use a solvent (tetraglyme) to make more available the fluoride ion, overcoming the lower reactivity of the internal double bond.

It was found that the principal by-product of the reaction is the ketone, deriving from the condensation of two molecules of olefin with a molecule of carbonyl fluoride; this by-product grows the yield in acyl fluoride, but it can be recycled and reused to produce other acyl fluoride, always in presence of the catalyst and enough amount of carbonyl fluoride.

Besides it is possible to underline (data not reported in the table) that working in analogous conditions (temperature, molar percentage of catalyst, carbonyl fluoride/olefin ratio) the more substituted is the carbon attacking the COF<sub>2</sub>, the lower is the reaction rate. This fact is easily explainable considering the steric hindrance. For the same reason, if the reactivity of the olefin decreases, also the amount of ketone decreases and the unreacted olefin increases.

2.2. Perfluorinated diacyl peroxides R<sub>1</sub>C(O)OOC(O)R<sub>2</sub>

In a typical run, a 150ml four-necked flask was equipped with mechanical stirrer, solid CO<sub>2</sub> condenser, thermometer and dropping funnel. The alkaline conditions were created dissolving NaOH in bi-distilled water, the solvent (CF<sub>3</sub>O)CF<sub>2</sub>O was added, the temperature of the system was lowered by an external cold bath to about 0°C, then the hydrogen peroxide was slowly introduced. Finally, the acyl fluoride was added drop by drop in about 1 minute by the dropping funnel. The exothermic value of the reaction was controlled by the cold bath, maintaining the temperature at about 0°C. When the IR analysis stopped to show the typical band of the -COF group of the acyl fluoride, the flask content was transferred into a separatory funnel and the organic phase was washed with distilled water until a neutral pH, then it was antyhydrated with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The peroxide concentration in CF<sub>3</sub>O)CF<sub>2</sub>O was determined by iodometric titration. The peroxide solutions have been characterized by IR and NMR analysis.



The work-up of the reaction is quite easy, because the low molecular weight of the starting acyl fluoride avoids the presence of annoying emulsions that make difficult the phase separation and are often cause of a low preparation yield.

As chlorofluorocarbon solvents are believed to contribute to the stratospheric burden of chlorine and the greenhouse effect, it has been verified that yields are not affected using perfluorinated solvents, like Galden D80 or LS-165, the choice depending on the foreseen use of the peroxide.

In the following table are reported the conditions of the synthesis and the relative yields.

Peroxide	Acyl-F (mmol)	NaOH (mmol)	H <sub>2</sub> O <sub>2</sub> (mmol)	Temp. (°C)	Reaction time (min)	Yield (%)
1	30	33	60	0°C	25	55
2	47	49	94	2°C	10	70
3	44	49	90	0°C	12	69
4	26	35	62	0°C	90	46

As it is possible to note, acyl fluorides having a reduced steric hindrance (2,3) are more reactive and shorter reaction times are required. This fact leads to higher yields in peroxide. On the contrary, acyl fluorides having a larger steric hindrance need longer reaction times and more easy go towards hydrolysis phenomena to the corresponding fluorinated acid, as it was verified by NMR analysis of the aqueous phase.

3. Thermal decomposition

In a typical kinetic measurement, about 1.5ml of peroxide solution were put in a glass test tube with screw neck, a whole set of these tubes was placed in a thermostat (± 0.1°C), and they were taken out at specified times and immediately frozen by dry ice temperature. The tubes were opened while cool, and exactly 1.0ml of the not decomposed peroxide solution was titrated by standard iodometry.

It has been verified that all four peroxides follow first-order kinetics in their decomposition, and for each temperature the decomposition rate constant k<sub>dec</sub> has been calculated. Besides, from decomposition rates at different temperatures the activation energy and the kinetic parameters have been calculated according to the well-known Arrhenius and Eyring equations. In the following tables all calculated data are reported, as well as data reported in the literature for known peroxides.

Peroxide	Temp. (°C)	k <sub>dec</sub> ·10 <sup>3</sup> (s <sup>-1</sup> )	Arrhenius		Eyring	
			ln(A)	E <sub>a</sub> (kcal/mol)	ΔH <sup>‡</sup> (kcal/mol)	ΔS <sup>‡</sup> (cal/molK)
1	60.0	3.0	34.5	29.8	29.1	7.9
	70.0	10.9				
	80.0	38.5				
2	60.0	4.4	35.0	29.8	29.1	8.7
	70.0	17.3				
	80.0	56.5				
3	20.0	1.8	37.7	28.3	27.7	14.3
	30.0	9.9				
	40.0	40.8				
4	5.0	1.8	37.3	26.8	26.2	13.8
	15.0	7.6				
	25.0	46.2				

Peroxide	Temp. (°C)	k <sub>dec</sub> ·10 <sup>3</sup> (s <sup>-1</sup> )	Arrhenius		Eyring	
			ln(A)	E <sub>a</sub> (kcal/mol)	ΔH <sup>‡</sup> (kcal/mol)	ΔS <sup>‡</sup> (cal/molK)
(CF <sub>3</sub> COO) <sub>2</sub> 5	45.0	1.6	30.9	26.5	25.9	0.7
	55.0	6.0				
	60.0	10.4				
(CF <sub>3</sub> CF <sub>2</sub> COO) <sub>2</sub> 6	25.0	1.2	31.5	24.6	24.0	2.1
	30.0	2.2				
	40.0	32.6				
(n-C <sub>4</sub> F <sub>7</sub> -COO) <sub>2</sub> 7	20.0	0.8	32.3	24.6	24.0	3.7
	30.0	9.9				
	40.0	40.8				
(n-C <sub>4</sub> F <sub>7</sub> )OOCF <sub>2</sub> (CF <sub>3</sub> COO) <sub>2</sub> 8	20.0	4.8	30.6	25.9	25.3	0.3
	30.0	19.6				
	40.0	71.6				
(c-C <sub>4</sub> F <sub>9</sub> -COO) <sub>2</sub> 9	20.0	0.8	30.6	25.9	25.3	0.3
	30.0	1.7				
	45.0	3.1				

In the literature it is reported the necessity to carry out the decomposition kinetics working with peroxidic solutions having low initial concentration (< 0.05M) to avoid auto-induced decomposition phenomena. We carried out our experimentation working at higher initial concentration (about 0.2-0.4M), reducing the error in determining the dye-tying point and improving the handling; however in the case of peroxide 1 it has been verified that high initial concentration doesn't invalidate the results. In the following table are reported the values obtained at different initial peroxide concentration: as it is possible to notice even reducing the initial concentration ten times, the k<sub>dec</sub> shows a maximum variation of 3% compared with the medium value.

Initial peroxide 1 concentration (M)	0.367	0.209	0.117	0.068	0.036
k <sub>dec</sub> ·10 <sup>3</sup> (s <sup>-1</sup> ) (at 64°C)	5.38	5.52	5.63	5.63	5.47

Observing tables 3 and 4, it is possible to notice that the activation enthalpies for decomposition of peroxides 1-4 are definitely higher than enthalpies of peroxides 5-9, being at most 3 kcal/mol lower than enthalpies of hydrogenated peroxides; also activation entropies are higher, indicating a more disordered transition state. The two facts justify the wide range of decomposition temperature, in fact for peroxides 1 and 2 the enthalpic contribute prevails, leading to high value of ΔG<sup>‡</sup> and consequent high temperature of decomposition; for peroxide 4 the entropic contribute prevails, leading to low ΔG<sup>‡</sup> value and consequent low temperature of decomposition, while for peroxide 3 the enthalpic and entropic contribute balances, leading to medium temperature of decomposition. In the following figure are reported the values of ΔG<sup>‡</sup> calculated from the values of ΔH<sup>‡</sup> and ΔS<sup>‡</sup> (obtained experimentally) in the range of temperature -20°C/+100°C.

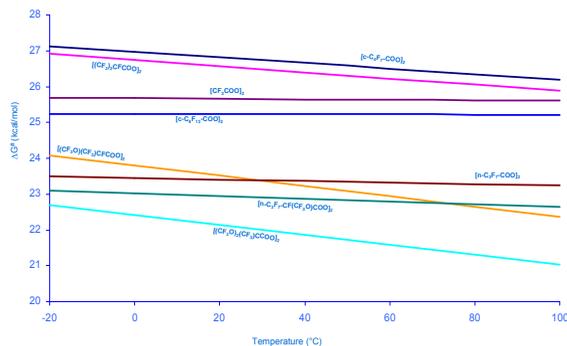
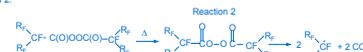


FIGURE 1

To simplify the comparison between peroxides, in the following table the calculated half-life times at 25°C are reported.

Peroxide	4	8	7	3	6	9	5	2	1
Half-life time (h)	0.46	1.9	4.3	4.6	16	95	195	850	1280
Relative half-life time to perox. 3	0.10	0.41	0.93	1	3.5	20.6	42	185	278

The thermal peroxide decomposition has been recognized as a concerted process involving the simultaneous homolysis of the C-C and O-O bonds, where the stability of the perfluoroalkyl radical is the crucial variable to determine the decomposition rate of the starting acylperoxide, Reaction 2.



The nature of the substituent bonded to the carbonyl of the acylperoxide is therefore an important variable on the homolytic decomposition rate of the peroxide.

The introduction of fluorine atoms in the  $\alpha$  position generally increase the stability of the end radicals and consequently the decomposition rate of the peroxide, whereas the introduction of fluorine atoms in  $\beta$  position is not so univocal. Pasto et al calculated that the introduction of one fluorine from difluoromethyl radical to trifluoromethyl radical determines a destabilization of the radical<sup>[2]</sup>; in fact trifluoroacetyl fluoride has a surprisingly high stability as compared to different perfluoroalkyl peroxides.

Those apparently conflicting data may be rationalized in terms of inductive, mesomeric and steric effect of the substituents directly bonded to the forming radical.

From the thermal decomposition parameters reported in Tables 3 and 4, it can be seen that with the introduction of a trifluoromethyl group in the  $\alpha$  position to the acylperoxide a consequent decrease of the decomposition rate has been observed, going from perfluoropropionyl peroxide 6 to perfluoro isobutyryl peroxide 2, in the reactions 3 and 4 respectively.



On the contrary introducing a trifluoromethoxy group in the identical  $\alpha$  position, the relative decomposition rate does not change dramatically from perfluoropropionyl peroxide 6 to perfluoro-2-methoxypropionyl peroxide 3. This behavior can be interpreted through the stabilization/destabilization effect of the substituents on the forming perfluoro radical. Both fluorine and trifluoromethyl radicals are characterized by a strong withdrawing inductive effect, destabilizing the radical, but fluorine radical may stabilize the forming radical through a positive mesomeric effect. This last stabilization may be more effective when a strong Sp<sup>2</sup> planar hybridization allows a larger degree of overlap between the SOMO of the forming radical and the fluorine lone pair. Therefore the two-trifluoromethyl groups destabilizing the forming radical cause a lower decomposition rate of the perfluoro isobutyryl peroxide as compared to perfluoropropionyl peroxide.

The trifluoromethoxy is similar to fluorine in the first substitution, but when also the second fluorine radical is substituted with a trifluoromethoxy radical as in the peroxide 4, a strong reduction of the decomposition rate is observable. This may be due to a high degree of planarity of the radical due to the bulkiness of the substituents, this planarity of the end radical allows a better overlap of the SOMO with the oxygen lone pair electrons of the two trifluoromethoxy substituents.



The planarity of the forming radical is therefore an essential factor in order to observe stabilization of the substituents on the radical center. This evidence can be also seen in the peroxide 1 that undergoes to the formation of a strained radical, centered on a secondary carbon atom on the cyclic structure like the perfluorocyclobutanyl radical deriving from peroxide 1.

In this case (reaction 6), the lack of overlapping due to the strained and unplanar perfluorocyclobutanyl radical may be a possible cause for the increase in temperature decomposition of 1 as compared to peroxide 9. The peroxide 9, like the peroxide 1, has the identical two CF<sub>3</sub> substituents in  $\alpha$  position to the forming radical, but in 9 the two CF<sub>3</sub> are part of a six member ring with a larger bond angle in comparison with the four member ring of the peroxide 1. This allows a better overlap of the SOMO with the  $\alpha$  fluorine lone pair electrons and a consequent higher stabilization of the cyclohexenyl forming radical from the peroxide 9.

4. Hydrolytic stability

The hydrolytic decomposition of perfluorodiacyl peroxides 1-4 have been investigated and the corresponding hydrolysis k<sub>dec</sub> are reported in table 7.

Peroxide	T (°C)	Thermolysis k <sub>dec</sub> x 10 <sup>3</sup> (s <sup>-1</sup> )	Hydrolysis k <sub>dec</sub> x 10 <sup>3</sup> (s <sup>-1</sup> )
1	70	10.9	12.3
2	70	17.3	21.1
3	30	9.9	7.9
4	15	7.6	7.3
7	15	1.5	4.5

As it is shown, for the  $\alpha$  branched peroxides 1-4 the hydrolytic reactions substantially don't interfere with the homolytic decomposition. On the contrary, working in identical conditions, for the linear perfluorobutyryl peroxide 7 an hydrolytic k<sub>dec</sub> three times higher than the anhydrolytic k<sub>dec</sub> was observed.

[1] H. Swada, Chem. Rev. 1996, 96, 1779  
[2] H. Swada and M. Nakayama, J. Fluorine Chem. 1998, 46, 423  
[3] Z. Chengyue et al., J. Org. Chem. 1982, 47, 2029  
[4] H. Swada et al., J. Appl. Polym. Sci. 1999, 72, 1101  
[5] D. Pasto, R. Kramarsky and C. Zacher, J. Org. Chem. 1987, 52, 3062

