1. Introduction

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

Their stability in the liquid phase and their reactivity in radical polymerization have been recognized since the early 1980s even though many studies have been done in hydrogenated radical chemistry recently.

Perfluoroalkylene peroxides have obtained a considerable interest and many have been studied in detail for different applications.

Among the different processes, the thermal decompositions of perfluorodiacyl peroxides is one of the more common methods to study other peroxide behaviors.

2. Synthesis

2.1. Perfluorodiacyl peroxides

Perfluorodiacyl peroxides can be prepared by the reaction between acyl halides (usually via chlorides) and hydrogen peroxide. The resulting peroxides are then washed with anhydrous NaOH solution.

3. Thermal decomposition

In the literature it is reported to carry out the decomposition kinetic with peroxide solutions having the initial concentration of 4 mmol/l [1], it is a method that involves the measurement of the solvent mass at a constant temperature, 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 and the organic phase was washed with anhydrous Na2SO4.


Table 1 shows the values obtained at different initial peroxide concentration: the reaction rate (kobs) decreases as the initial concentration decreases, indicating a more disordered transition state. The two facts justify the wide range of decomposition temperature, in fact for peroxides 1 and 4, the temperature of decomposition is about 100°C, while for peroxides 2 and 3, the temperature is about 20°C.

To simplify the comparison between peroxides, in the following table the calculated half-life times at 100°C are reported.

Table 2 shows the peroxide decomposition temperatures and half-life times at 100°C.

On the contrary introducing a trifluoromethoxy group in the peroxide structure (reaction 6), the lack of overlapping due to the strained and unplanar degree of overlap between the SOMO of the forming radical and the oxygen lone pair electrons of the two trifluoromethoxy groups decreases, also the amount of the unreacted molecule of carbonyl fluoride; this by-product lowers the yield in acyl chlorides.

3.3. Hydrolysis

The hydrolytic decomposition of perfluorodiacyl peroxides shows a high temperature dependence.

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4. Hydrolysis stability

The thermal decomposition of perfluorodiacyl peroxides 1,2 have been investigated and the corresponding hydrolysates 3,4 are reported in table 3.

As it is shown, for the branched peroxides 1-4 the hydrolysates normally do not form the characteristic product.

The hydrolysate of peroxides 1-4 is a solution of acyl fluoride and a mixture of perfluoride and hydrogen fluoride, in the case of peroxides 1-2 this mixture is not extractable, this behavior is due to the lower volatility of the hydrolysates 3,4 compared to the peroxide 1-2.

4.2. Perfluorodiacyl peroxides

In this work the decomposition of perfluorodiacyl peroxides has been investigated using the technique of liquid phase hydrolysis. The results obtained show that the hydrolysis rate is not influenced by the presence of a trifluoromethoxy group in the peroxide structure.

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