

E₁₅

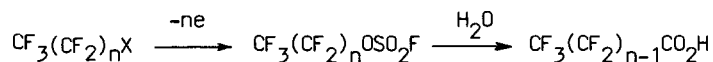
INDIRECT ELECTROCHEMICAL OXIDATION OF PRIMARY PERFLUORINATED ORGANIC COMPOUNDS IN FLUOROSULFURIC ACID

Alain Germain*, Daniel Brunel and Patrice Moreau

U.A.-C.N.R.S. 1097, Institut de Chimie Fine, Université des Sciences et Techniques du Languedoc, Place E. Bataillon, 34060 Montpellier Cédex (France)

Organic perfluorinated compounds are extremely difficult to oxidize. Consequently, the direct electrochemical oxidation of most of them is not effective, even in perfluorinated sulfonic acids which are exceptional solvents for anodic oxidation. However, indirect oxidations can be performed in fluorosulfuric acid.

We report such oxidations of primary linear perfluorinated compounds $\text{CF}_3(\text{CF}_2)_n\text{X}$, with $\text{X} = \text{H}, \text{Br}, \text{CH}_2\text{OH}, \text{CO}_2\text{H}$ and SO_3H . In all cases, a perfluoroalkane fluorosulfate, $\text{CF}_3(\text{CF}_2)_n\text{OSO}_2\text{F}$, is obtained in mild conditions and good yields. Alkaline hydrolysis of these esters leads to carboxylic acids $\text{CF}_3(\text{CF}_2)_{n-1}\text{CO}_2\text{H}$. Starting from α, α, β -trihydrylperfluoroalcohols $\text{H}(\text{CF}_2)_n\text{CH}_2\text{OH}$, dicarboxylic acids $(\text{CF}_2)_{n-2}(\text{CO}_2\text{H})_2$, are synthesized.



In every case, the observation of C.I.D.N.P. in fluorine N.M.R. spectra, during the electrolysis, confirms the indirect process via the formation of the peroxodisulfonyl difluoride $(\text{FSO}_3)_2$. The application of Kaptein's rules signifies the encounter of freely diffusing radicals leading to a radical pair (F-type).

The number of electrons which are involved depends on the nature of X.

A discussion is presented in each case about the mechanism which is suggested by these results.