Journal of Fluorine Chemistry 132 (2011) 107–113

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Products formed at intermediate stages of electrochemical perfluorination of propionyl and n-butyryl chlorides. Further evidence in support of NiF_3 mediated free radical pathway

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ARTICLE INFO

Article history:
Received 7 October 2010
Received in revised form 10 November 2010
Accepted 3 December 2010
Available online 10 December 2010

Keywords:
Electrochemical fluorination
Propionyl chloride
n-Butyryl chloride
HF soluble intermediates
Free radical mechanism
Perfluorination

ABSTRACT

The partially fluorinated HF soluble intermediates formed during the electrochemical perfluorination of propionyl chloride (PC) and n-butyryl chloride (n-BC) were analyzed after passing 0%, 25%, 50%, 75% and 100% of theoretical charge required for the fluorination of PC and n-BC. The acid fluorides formed were converted to their corresponding sodium salt by alkali treatment and were separated by methanol extraction. The methanol was subsequently removed from the extract by vacuum distillation and the residue containing partially fluorinated sodium carboxylates was analyzed using ^{19}F and ^{1}H NMR spectra. Initial perfluorination on activated electrode surface indicates the operation of 'zipper-mechanism'. Formation of partially fluorinated product mixture, initial selectivity towards primary and secondary carbon, carbon chain isomerization and formation of cleaved and coupled products support the general operation of free radical pathway in the overall electrochemical process.

1. Introduction

Electrochemical perfluorination of propionyl and n-butyryl fluorides is well known for many decades [1,2]. Gambaretto et al. [2], suggested EC_bEC_N mechanism for electrochemical fluorination process. Dimitrov and co-workers in a fairly detailed investigation mainly involving electrochemical perfluorination (ECPF) of trialkylamine have established formation of many partially fluorinated intermediates in this process [3–7]. The HF soluble partially fluorinated intermediates were isolated at different stages of ECPF [3,6,7]. Many studies by Dimitrov et al. [5–8], Sartori et al. [9–11], and Velayutham et al. [12] also confirmed the free radical pathway. Since anodically activated nickel is the only electrode in ECPF process, the involvement of high valent nickel fluoride species such as NiF_3 and NiF_4 in ECPF process has been suggested by Ignat'ev et al. [9,11,13]. In an interesting experiment, fluorinated products were obtained under open circuit conditions on an anodically polarized NiF_3 surface [9]. Free radical pathway involving a cyclopropane intermediate was also suggested to explain the carbon chain isomerization during ECPF of alkane sulphonic acid [13] and alkane carboxylic acid fluorides [12,14].

Partially fluorinated compounds were found as minor constituents in the perfluorination products during ECPF in a number of investigations cited above. However, analysis of partially fluorinated compounds dissolved in the HF phase at different stages of electrolysis is not quite commonly attempted. The ECPF of triethylamine reported by Dimitrov et al. [7] and Hollitzer and Sartori [15] appears to be the only study of this kind. This approach is adapted here for the ECPF of propionyl (PC) and n-butyryl chloride (n-BC) by systematically analyzing the HF phase at different stages of electrolysis. Since the perfluorinated products such as perfluoropropionyl fluoride (bp = −30 °C) and perfluoro-n-butyryl fluoride (bp = 5 °C) are highly volatile [16], they do not remain in the HF phase. This allows convenient draining of HF phase and comprehensive analysis of even trace levels of fluorinated compounds in the HF phase.

2. Results and discussion

Typical partially fluorinated and perfluorinated carboxylic acid salts obtained at different stages of ECPF of PC are presented in Table 1. The product selectivity values presented in this table are calculated based on the ^{19}F NMR signal intensities obtained at each

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doi:10.1016/j.jfluchem.2010.12.004