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ORIGINAL PAPER

Anodic oxidation of alkane carboxylates and perfluoroalkane carboxylates at platinum and graphite anodes: product selectivity and mechanistic aspects

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Abstract Constant current electrolysis of sodium octanoate produced Kolbe and non-Kolbe products. Dimer is the major product at Pt anode and non-Kolbe products were formed on graphite anode. Influence of quantity of electricity, current density, and nature of electrode was studied. Under optimized experimental conditions, butanoate, perfluorooctanoate, and perfluorobutanoate were electrolyzed. Major and minor products were identified based on GC–MS spectra. Isomeric products are due to cationic rearrangement by 1,2-hydride shift and selectivity among them are also rationalized. Anodic decarboxylation of perfluorobutanoate and perfluorooctanoates gave Kolbe dimer on platinum electrode. The role of solvent and criteria for choice of radical or cationic pathway has been discussed.

Keywords Anodic oxidation · Alkane carboxylates · Perfluoroalkane carboxylates · Kolbe product, non-Kolbe product · Rearrangement · 1,2-Hydride shift

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Introduction

Oxidation of organic compounds requires vigorous experimental conditions such as high temperature and pressure. Oxidation reactions also use aggressive chemicals as oxidizing agents which may pollute the environment. Electroorganic synthesis has attracted much interest as an environmentally friendly method because electrons are inherently environmentally friendly reagents compared with conventional oxidizing and reducing reagents [1]. Kolbe reaction is a well-known carbon–carbon bond-forming reaction [2] and has been well studied because of its importance in electrochemical synthesis for the formation of a wide variety of organic compounds [3–7]. Depending on experimental parameters and structure of carboxylates, the reaction products are derived either from radical or carbocation, and are called Kolbe or non-Kolbe reaction, respectively [3, 4]. A.K. Vijh et al. have extensively reviewed the kinetics and mechanism of Kolbe reaction [5]. In general, Pt anode favors a one-electron transfer to give free radical derived products. Graphite, on the other hand, favors a two-electron transfer to give a cationic derived product which is due to strong adsorption of free radical formed and thus promote further oxidation to carbonium ion [8]. T. Tajima et al. have recently developed a novel electrolytic system for successful application in Kolbe and non-Kolbe reactions using easily separable and reusable solid-supported bases [1, 9–13]. Trifluoromethylated organofluorine compounds have attracted increased attention for medicinal and agricultural applications. Hence, electrochemical decarboxylation of perfluorocarboxylic acids is focused towards anodic trifluoromethylation of olefins [14–18]. S. Swann and F.H. Baastad have reported the synthesis of half fluorinated hydrocarbons and half