

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

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. Vijn 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

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Table 1 Results of anodic oxidation of sodium octanoate and perfluorooctanoate at Pt anode in aqueous methanol (40% v/v) medium

Run	1	2	3	4	5	6	7 ^a	8 ^b	9 ^{a,b}
Electricity passed (F/mol)	1	2	4	10	4	4	4	4	4
Current density (mA/cm ²)	200	200	200	200	400	600	400	400	400
Conversion (%)	30.0	58.2	61.7	66.4	58.4	58.1	38.6	1.0	1.6
Isolated yield (%) ^c	22.3	88.3	98.0	90.7	97.0	96.2	17.1 ^d	–	–

Electrolyte: LiClO₄ (10 mol%)

^a Graphite electrode

^b Sodium perfluorooctanoate as starting material

^c Yield based on dimer formation

^d Yield based on 2-heptanol formation. Runs 1–6 and 8=Pt anode

fluorinated ester by mixed Kolbe electrolysis of potassium salt of butyric and perfluorobutyric acid, potassium salt of nonanoic and perfluorooctanoic acid, and potassium salt of monoethyl sebacate and perfluorobutyric acid [19]. Electrochemical decarboxylation of higher homologs of perfluorocarboxylic acids are scanty [20–23]. Here, an attempt has been made to study the electrodecaboxylation of octanoic acid, butyric acid, perfluorobutyric acid, and perfluorooctanoic acid. This study may throw some light on the feasibility of electrodecaboxylation of the perfluoro acids, nature of products, mechanism, etc. Influence of experimental parameters, such as quantity of electricity, current density, and nature of electrodes on Kolbe and non-Kolbe products, is discussed. Products were identified and mechanism of their formation is discussed. Electrolysis products were analyzed by GC–MS technique and the results are discussed in detail.

Experimental

Chemicals and apparatus

All starting materials were commercially available and were used as received. Sodium salt of carboxylates were

prepared by a procedure described in the literature [14]. ¹H NMR spectra were recorded with a 400-MHz Bruker NMR spectrometer with CDCl₃ and TMS as solvent and reference, respectively. ¹⁹F NMR (376.5 MHz) was recorded using CFCl₃ as reference. Crude electrolysis products were subjected to GC–MS analysis using Agilent 5975 C GC/MSD with triple-axis HED-EM detector and 7890 A GC.

The electrolysis apparatus is made up of undivided polypropylene beaker of about 25 ml capacity. Platinum (Pt) and graphite (Gr) electrodes of working area 2.0 cm² are placed 0.5 cm apart. Aqueous methanol (40% v/v) and lithium perchlorate salt were used as solvent and supporting electrolyte, respectively. GC–MS data of the identified compounds are given in the [Electronic supplementary material](#).

Electrolysis of sodium carboxylates

About 15.0 ml aqueous methanolic (40% v/v) solution of sodium octanoate (1.662 g, 10 mmol) was taken in an electrolytic cell. The electrolysis was carried out under galvanostatic condition using a Pt anode at a current density of 400 mA/cm² at 25±2 °C until 4 F was consumed (Table 1, run 5). The temperature of the cell was kept constant during electrolysis using an ice bath.

Table 2 Product selectivity based on GC–MS analysis

Run Product	1	2 ^a	3	4	5 ^b	6	7 ^c	8
	Selectivity (%)							
Tetradecane (dimer) (I)	66.2	63.4	61.4	57.4	38.3	46.2	–	–
Dodecane (II)	0.8	1.9	2.1	2.6	3.2	3.8	–	–
1-Heptanol (III)	2.2	1.7	2.2	3.0	4.6	3.8	6.5	–
2-Heptanol (IV)	8.0	–	9.7	11.6	–	18.7	19.5	–
Methyl octanoate (V)	2.7	2.0	2.4	2.6	3.8	2.1	2.5	–
1-Heptyl octanoate (VI)	3.6	4.4	3.1	2.6	4.3	2.7	2.8	–
2-Heptyl octanoate (VII)	8.8	11.1	8.9	8.5	8.7	6.5	4.5	–
3-Heptyl octanoate (VIII)	5.8	7.9	1.5	6.4	6.4	5.0	4.0	–
4-Heptyl octanoate (IX)	1.9	3.2	2.2	2.3	3.1	1.8	0.4	–
Perfluorotetradecane (XIV)	–	–	–	–	–	–	–	100

^a 3.0% heptanal (XII) was identified

^b 15.32% heptyl methyl ether (X) was identified

^c 49.1% and 4.0% of octanoic acid (XI) and 1-tetradecene (XIII) were identified, respectively

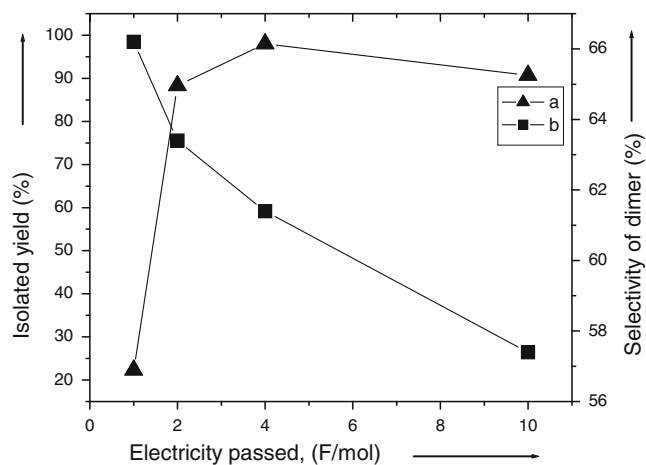


Fig. 1 Influence of electricity passed (F/mol) on **a** isolated yield of the electrolysis product and **b** selectivity of Kolbe product

After the electrolysis was completed, the oily upper layer was separated using a separating funnel and aqueous layer was diluted with water. This aqueous solution was extracted twice (15 ml) with ether solvent and combined with liquid product. The combined extract was subjected to water wash, brine wash, and finally dried with anhydrous sodium sulfate. Solvent was evaporated under vacuum to get crude product. The crude product was analyzed by NMR and GC–MS techniques.

Similar experiments were carried out with sodium butanoate (1.1 g, 10 mmol), sodium perfluorooctanoate (0.5 g, 1.15 mmol), and sodium perfluorobutanoate (0.5 g, 2.1 mmol) at both Pt and Gr anodes.

Results and discussion

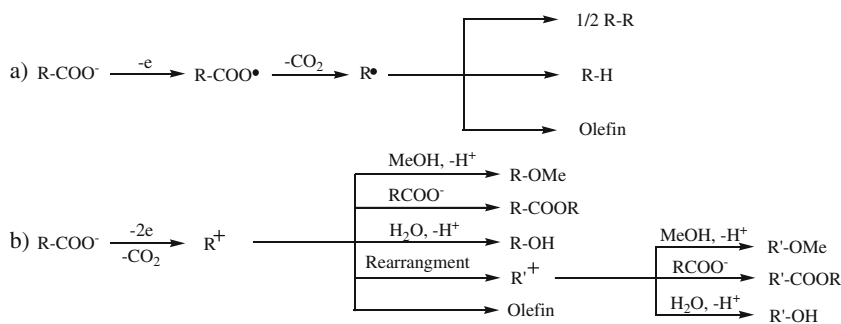
Anodic decarboxylation of sodium octanoate and perfluorooctanoate

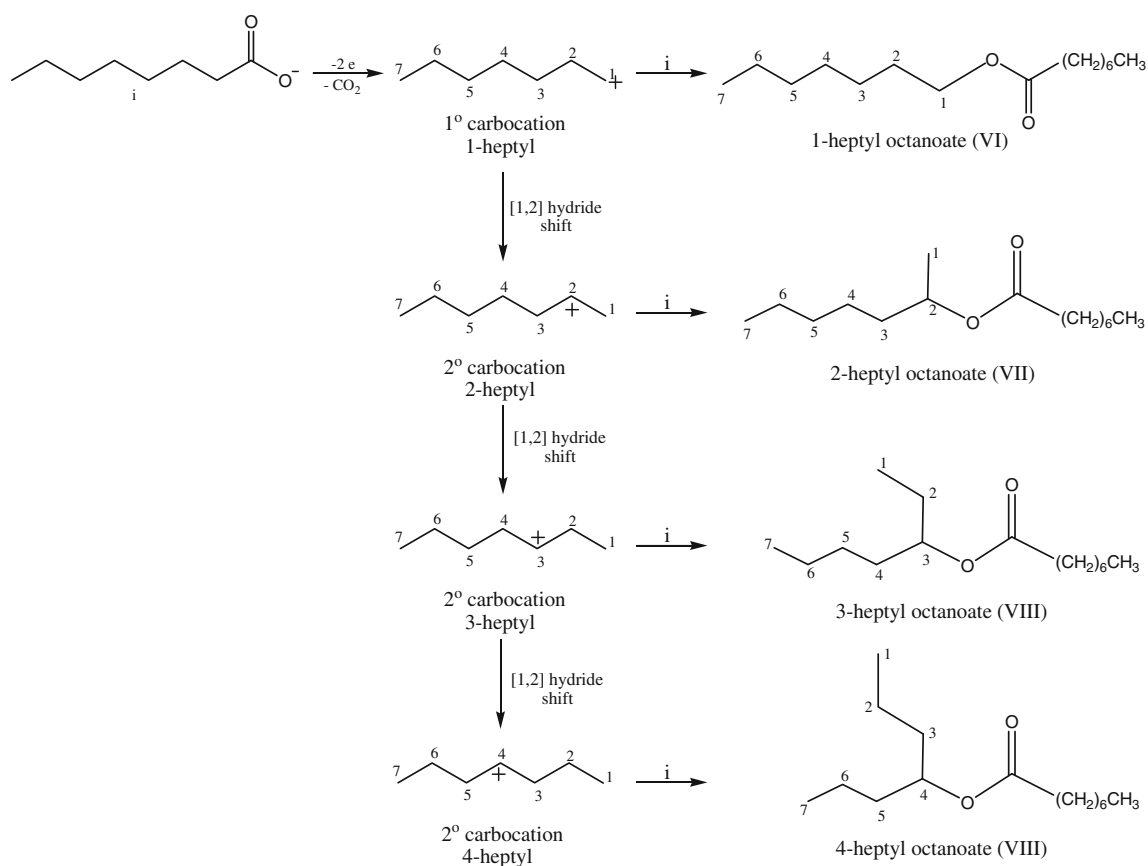
Anodic oxidation of sodium octanoate and sodium perfluorooctanoate was carried out in aqueous methanol medium using platinum and graphite anodes. Electrochemical decarboxylation products were obtained from

both one- and two-electron oxidations. Results of electrochemical oxidation are given in Table 1. The selectivity of Kolbe and non-Kolbe products obtained from anodic oxidation of octanoate in aqueous methanol under different current densities is given in Table 2. The influence of quantity of electricity (F/mol) passed on isolated yield of the electrolysis product and the selectivity of Kolbe product are shown in Fig. 1. Yield of the electrolysis product increases with the increase in quantity of electricity passed, but the selectivity of the Kolbe product decreases. On the other hand, the selectivity of the non-Kolbe products has been increased. Pt electrode normally favors a one-electron oxidation reaction; however, it gave two-electron oxidation products of about 40% (run 4) when increasing the quantity of electricity passed otherwise under identical conditions. A general reaction Scheme 1 shows the possible reaction products through radical and cationic intermediates by one- and two-electron transfer, respectively. Electrolysis products were subjected to GC–MS analysis and identified.

Influence of the anodic current density on the isolated yield and selectivity of the Kolbe product is shown in Fig. 2. There is no significant change in the yield of the isolated product when the anodic current density is increased from 200 mA cm⁻² to 600 mA cm⁻². Selectivity of the non-Kolbe products increases considerably and the dimer decreases (Table 2) with the increase in current density. Heptyl methyl ether (X, 15.3%) and 2-heptanol (IV, 18.7%) are formed considerably high in runs 5 and 6, respectively. It is very interesting to observe that a minor percentage of dodecane (II, 3.2%, run 5) was identified in the reaction mixture. The formation of this unusual product (dodecane II) can be demonstrated by the further successive oxidation of intermediate product formed in the electrolysis mixture as shown in reaction Scheme 2. About 3.0% heptanal (XII) was identified in run 2 that may be formed through either by hydrolysis of dimethyl acetal of heptanal which may be formed from two-electron oxidation of heptyl methyl ether (X) or by one-electron product arising from the reaction between heptyl radicals and molecular oxygen [24]. Dimethyl acetal of

Scheme 1 General reaction pathway of **a** one-electron and **b** two-electron decarboxylation of alkane carboxylates





Scheme 3 Formation of four isomeric heptyl octanoates by rearrangement of initially formed 1-heptyl cation through successive 1,2-hydride shift

including molecular ion peaks, were observed at m/e 242 $[M]^+$, 227 $[M-CH_3]^+$, and 213, 199, 185, 171, 157 by the loss of 14 mass units.

The mass spectra of the other three isomeric heptyl octanoates are quite similar where the base peak found at

m/e 127 corresponds to $CH_3(CH_2)_5CH_2C\equiv O^+$, whereas the base peak of 1-heptyl octanoate is found at m/e 145. All other diagnostic peaks are found to be the same as in 1-heptyl octanoate. The position of the heptyl chain in isomeric heptyl octanoate can be established by examining

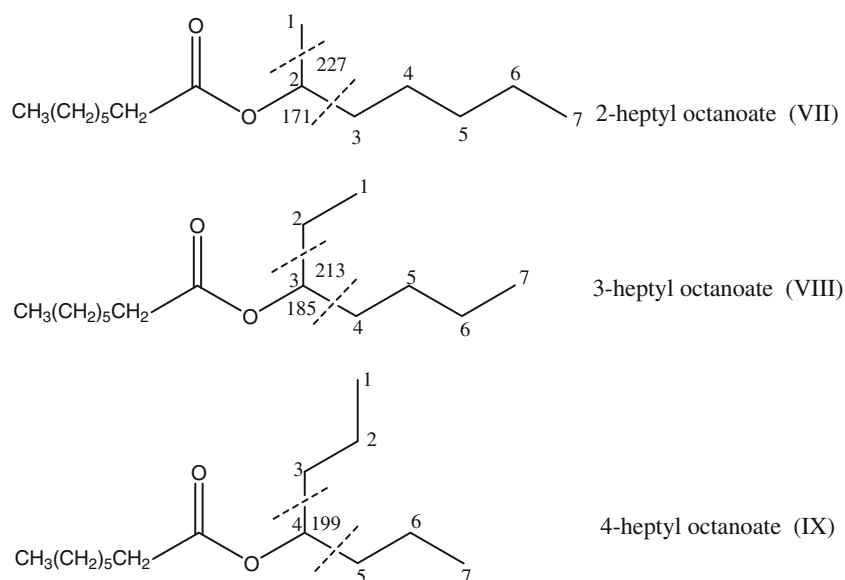


Fig. 3 Pattern of fragmentation at branching of heptyl chain

gave only non-Kolbe products, which may be due to the influence of added additive lithium perchlorate. Ethyl propyl ether was formed about 22.5% at graphite anode. The formation of this ether may be elucidated according to Scheme 4 by the nucleophilic attack of *n*-propanol to ethyl cation formed by the oxidation of propionic acid in a similar way described in reaction Scheme 2.

Electrochemical oxidation of sodium perfluorobutyrate in aqueous methanol at both Pt and graphite anodes produced heptafluorobutanol (XXII). This identified product may be possible by the combination of perfluoropropyl radical and CH₂OH radical generated at the anode [3]. The conversion is low due to competing oxygen evolution [27] in aqueous solution with decarboxylation of sodium butanoate and perfluorobutanoate. Perfluorobutanoate was electrochemically oxidized in anhydrous MeOH–MeONa–Pt and MeOH–Et₃N–Pt system, giving perfluorohexane with the yield of about 70% and 22%, respectively.

Conclusions

The present study reveals that the quantity of electricity passed increases the conversion from 30% to 66% on Pt anode. However, the selectivity of Kolbe products at Pt electrode decreases from 66% to 57% with the increase in electricity passed. Platinum electrode gives products derived from both Kolbe and non-Kolbe intermediates. There is no marked influence of anodic current density on the yield of the electrolysis product. Even in the Pt electrode, large excess quantity of electricity passed led to further oxidation of radical intermediate to cation intermediate, and hence non-Kolbe products were obtained. Cation derived from two-electron oxidation has suffered by 1,2-hydride shift that led to rearrangement products, and their selectivity can be explained by the stability of the carbocations. Oxidation of sodium octanoate in graphite anode gives only non-Kolbe products. No dimer was obtained. Oxidation of perfluorooctanoate on Pt exclusively produced dimer. However, low conversion is due to adsorption of solid dimer on the anode which prevents further oxidation of carboxylates. Anodic discharge of perfluorooctanoate was not observed in graphite anode and only gas evolution was noticed. Perfluorocarboxylates gave radical intermediate products only. It could not be possible to remove a second electron from a radical intermediate due to the electron-withdrawing nature of fluorine atoms.

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