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# 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

Run	1	2	3	4	5	6	7 <sup>a</sup>	8 <sup>b</sup>	9 <sup>a,b</sup>
Electricity passed (F/mol)	1	2	4	10	4	4	4	4	4
Current density (mA/cm <sup>2</sup> )	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 (%) <sup>c</sup>	22.3	88.3	98.0	90.7	97.0	96.2	17.1 <sup>d</sup>	_	-

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

Electrolyte: LiClO<sub>4</sub> (10 mol%)

<sup>a</sup> Graphite electrode

<sup>b</sup> Sodium perfluorooctanoate as starting material

<sup>c</sup> Yield based on dimer formation

<sup>d</sup> 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 electrodecarboxylation of octanoic acid, butyric acid, perfluorobutyric acid, and perfluorooctanoic acid. This study may throw some light on the feasibility of electrodecarboxylation 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]. <sup>1</sup>H NMR spectra were recorded with a 400-MHz Bruker NMR spectrometer with CDCl<sub>3</sub> and TMS as solvent and reference, respectively. <sup>19</sup>F NMR (376.5 MHz) was recorded using CFCl<sub>3</sub> 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  $2.0 \text{ cm}^2$  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/cm<sup>2</sup> 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 Selecti	2 <sup>a</sup> vity (%)	3	4	5 <sup>b</sup>	6	7 <sup>c</sup>	8
	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	-
a 2 0% hortanal (XII) was	Methyl octanoate (V)	2.7	2.0	2.4	2.6	3.8	2.1	2.5	-
identified	1-Heptyl octanoate (VI)	3.6	4.4	3.1	2.6	4.3	2.7	2.8	-
<sup>b</sup> 15.32% heptyl methyl ether (X) was identified	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	-
<sup>c</sup> 49.1% and 4.0% of octanoic	4-Heptyl octanoate (IX)	1.9	3.2	2.2	2.3	3.1	1.8	0.4	-
acid (XI) and 1-tetradecene (XIII) were identified, respectively	Perfluorotetradecane (XIV)	-	-	-	-	-	-	_	100

Table based



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 vield 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<sup>-2</sup> to 600 mA cm<sup>-2</sup>. 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 twoelectron oxidation of heptyl methyl ether (X) or by oneelectron 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





Fig. 2 Influence of anodic current density  $(mA/cm^2)$  on **a** isolated yield of the electrolysis product and **b** selectivity of Kolbe product

heptanal has not been identified in any run owing to hydrolysis of acetal to aldehyde in aqueous methanol. Heptanal (XII) thus formed may further be oxidized successively into heptanoic acid and dodecane at Pt electrode.

The influence of graphite anode on the selectivity of products formed from the decarboxylation of octanoate has been carried out under identical experimental conditions as in run 5. It is observed that no dimer (radical intermediate) was identified even in traces. Graphite electrode gave only those products derived from cationic intermediate along with about 49.0% of starting material that was recovered as octanoic acid (XI) from the reaction mixture. It is interesting to observe the formation of octanoic acid (XI), 1-tetradecene (XIII), and the methyl octanoate (V) from electrolysis of sodium octanoate in all the runs [8]. 2-Heptanol (IV) (19.6%) was formed in major quantity as a rearrangement product (Table 2). But the isolated yield is low which may be due to predominant oxygen evolution reaction at the graphite anode. It may be concluded that graphite electrode favors two-electron oxidation (non-Kolbe) products irrespective of the carbon chain length of the starting material. It is well known that the Pt electrode prefers radical or cationic

Scheme 2 Formation of dodecane from octanoate by successive oxidation of methyl heptyl ether

pathway depending mainly on the structural features of carboxylic acid and inert salts as additives to achieve and enhance the yield of cation-derived products [9, 11, 25, 26]. To examine the electron withdrawing nature in the structure of carboxylate on the yield and the electrolysis product, perfluorooctanoate was taken and electrolyzed under similar experimental conditions as in run 5. Perfluorooctanoate underwent decarboxylation to give perfluorotetradecane (XIV, dimer) by radical pathway, and the reaction was ceased due to deposition of perfluorotetradecane as white crystals (obs. mp=98-102 °C; rept. mp=99-101 °C [27]) on the surface of the Pt electrode [21, 22], which is usually known as anode fouling, and oxygen evolution competes with the Kolbe reaction [28]. GC-MS analysis showed that perfluorotetradecane is the only product. This implies that the radical pathway is solely operated in perfluoroalkane carboxylates. It could not be possible to oxidize perfluoroalkyl radical to cation due to strong electron-withdrawing nature of fluorine atom under these experimental conditions.

Rearrangement during electro decarboxylation of sodium octanoate

It is intriguing to observe that there have been four isomeric heptyl octanoates (VI, VII, VIII, and IX) obtained which can be readily be explained by the nucleophilic attack of octanoate on 1-heptyl and rearranged heptyl cations produced by the two-electron oxidation of octanoate as shown in Scheme 3.

These four isomeric heptyl octanoates' structural assignment is confirmed by the mass spectrum. It has been found that the mass spectrum of 1-heptyl octanoate (VI) generally has a base peak at m/e 145 due to protonated octanoic acid (CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>C(=OH<sup>+</sup>)OH) [29] fragmented by β-hydrogen abstraction from alcoholic alkyl chain that led to McLafferty-type rearrangement and subsequent hydrogen abstraction from alkene chain, which confirms the presence of octanoate moiety. Furthermore, octanoate and heptyl chain can also be confirmed by diagnostic peaks found at m/e 98, 115, and 127 corresponding to CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sup>-</sup>-CH<sub>2</sub><sup>+</sup>, CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>-O<sup>+</sup>, and CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>C=O<sup>+</sup>, respectively. Successive fragmentation peaks of very low intensities,

a) 
$$C_6H_{13}$$
-CH<sub>2</sub>-COONa  $\xrightarrow{-2e}$   $C_6H_{13}$ -CH<sub>2</sub>  $\xrightarrow{-H^+}$   $C_6H_{13}$ -CH<sub>2</sub>-OCH<sub>3</sub>  $\xrightarrow{-2e}$   $C_6H_{13}$ -CH<sub>2</sub>-OCH<sub>3</sub>  
 $-H^+$   $(X)$   $-H^+$   $(X)$   
 $C_{12}H_{26}$   $\xrightarrow{-1e}$   $C_6H_{13}$ -COOH  $\xrightarrow{[O]}$   $C_6H_{13}$ -CHO  $\xrightarrow{-H^+}$   $C_6H_{13}$ -CHO(OCH<sub>3</sub>)<sub>2</sub>  
(II)  $C_{12}H_{26}$   $\xrightarrow{-1e}$   $C_6H_{13}$ -COOH  $\xrightarrow{-1e}$   $C_6H_{13}$ -COOH  $\xrightarrow{-1e}$   $C_6H_{13}$ -CHO  $\xrightarrow{-1e}$   $C_6H_{13$ 

CH.OH



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]<sup>+</sup>, 227 [M–CH<sub>3</sub>]<sup>+</sup>, 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<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>C≡O<sup>+</sup>, 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

Run	Anode	Yield <sup>a</sup> (%)	Product selectivity (%) <sup>b</sup>								
			1- Propanol (XV)	Methyl butyrate (XVI)	1-Propyl butyrate (XVII)	2-Propyl butyrate (XVIII)	2-(2-Propoxy) ethanol (XIX)	1,1-Dimethoxy propane (XX)	Ethyl propyl ether (XXI)		
1 2	Pt <sup>c</sup> Gr <sup>c</sup>	21.5 21.0	13.4 12.3	6.3	9.8 9.8	24.3 20.3	3.6 2.4	2.0 1.7	8.4 22.5		

Table 3 Results of anodic oxidation of sodium butyrate in aqueous methanol (40% v/v) medium

Electrolyte: LiClO<sub>4</sub> (10 mol%)

<sup>a</sup> Isolated yield based on 2-propyl butyrate

<sup>b</sup> Selectivity based on GC-MS data

<sup>c</sup> 4 F/mol charge passed; current density-400 mA/cm<sup>2</sup>

the fragmentation at the branching position. Peaks found at m/e 227 and 171 are due to fragmentation at branching by cleavage at methyl and pentyl groups, respectively, which reveals that the octanoate might be at 2-position of the heptyl chain. Similarly, peaks found at m/e 213 and 185 are due to fragmentation at branching by cleavage of ethyl and butyl groups, respectively, which reveals that the octanoate may possibly be at 3-position of heptyl group. Only one fragmentation peak due to branching is found at m/e 199 which corresponds to loss of symmetrical propyl group,

revealing that octanoate might be at 4-position in the heptyl chain. The cleavage patterns at branching are shown for convenience in Fig. 3.

These rearrangement products can be readily understandable by the initially formed 1-heptyl cation that undergoes consecutive 1,2-hydride shift [30-33] due to availability of vacant orbital, giving more stable 2° carbocation over 1° carbocation. It is obvious that this rearrangement may possibly occur through 1,2-migration. The order of stability of the heptyl cations is shown below.

$$\overset{7}{\text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\overset{2}{\text{C}}\text{H}_{2}\text{CH}_{3} \\ > \overset{7}{\text{CH}_{3}\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{L}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{L}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{L}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{L}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{L}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{C}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{C}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{C}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{C}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{C}}\overset{1}{\text{C}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{C}}\overset{1}{\text{C}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{C}}\overset{1}{\text{C}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{5}{\text{C}}\overset{4}{\text{C}}\overset{3}{\text{C}}\overset{2}{\text{C}}\overset{1}{\text{C}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{7}{\text{C}}\overset{1}{\text{C}}\overset{7}{\text{C}}\overset{6}{\text{C}}\overset{7}$$

The product selectivity (Table 2) among these four isomeric heptyl octanoates also reflects the stability order. Of the four isomers, 2-heptyl octanoate (VII) is formed predominantly in all runs. For instance, in run 1, the ratio of the four isomeric heptyl octanoates is about 1.9:4.6:3:1 from compounds VI, VII, VIII, and IX, respectively.

Anodic decarboxylation of sodium butanoate and perfluorobutanoate

In order to examine the product distribution of lower aliphatic acid under identical experimental conditions as in run 5 (Table 1), butanoate was electrolyzed in both Pt and Gr electrodes. Results are shown in Table 3. In this case, Kolbe dimer is not identified in both Pt and Gr electrodes, and only those products derived from cationic intermediate have been formed. There is no significant difference in the isolated yield of electrolyzed product both in Pt and graphite. W.J. Koehl [34] has reported that electrolysis of butyric acid at carbon anode in aqueous solution gave propene (47%), cyclopropane (25%), and 12% of mixture of *n*-propyl and isopropyl butyrate (about 1:2 ratio). Moreover, the yield is only based on the products isolated from the reaction mixture. Pt anode also

$$CH_{3}CH_{2}CH_{2}COONa \xrightarrow{-2e} CH_{3}CH_{2}CH_{2}^{+} \xrightarrow{MeOH, -H^{+}} CH_{3}CH_{2}CH_{2}^{-OCH_{3}} \xrightarrow{-2e, 2 - H^{+}} CH_{3}CH_{2}CH_{0}CH_{3})_{2} \xrightarrow{(XX)} H_{2}O \xrightarrow{(XX)} H_{2}O \xrightarrow{(XX)} CH_{3}CH_{2}CH_{2}^{+} \xrightarrow{-2e} CH_{3}CH_{2}COOH \xrightarrow{[O]} CH_{3}CH_{2}CH_{0}OH \xrightarrow{(XX)} CH_{1}CH_{1}OH \xrightarrow{(XX)} CH_{1}OH \xrightarrow{(XX)} CH_{1}OH$$

Scheme 4 Formation of ethyl propyl ether from butyrate by successive oxidation of methyl propyl ether

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 CH<sub>2</sub>OH 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–Et<sub>3</sub>N–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 electronwithdrawing nature of fluorine atoms.

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