Journal of Electroanalytical Chemistry 638 (2010) 39–45

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Galvanostatic and potentiostatic fluorination of 2-indanone, 1-indanone and 1,3-indandione in $Et_3N \cdot 4HF$ medium. Adsorption effects on yield and product selectivity

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A R T I C L E I N F O

Article history:
Received 29 July 2009
Received in revised form 8 October 2009
Accepted 14 October 2009
Available online 20 October 2009

Keywords:
Anodic fluorination
2-Indanone
1,3-Indandione
Chronoamperometry
$Et_3N \cdot 4HF$

A B S T R A C T

Selective electrochemical fluorination (SEF) of 1-indanone, 2-indanone and 1,3-indandione were carried out in $Et_3N \cdot 4HF$ ionic liquid. Cyclic voltammetric measurements indicated that the ionic liquid undergoes oxidation below 2 V on platinum electrode while the background limit is extended up to 2.3 V on glassy carbon electrode. Well defined voltammetric peaks were observed for all the three compounds on glassy carbon electrode. Significant absorption effects were also noticed. Preparative electrolysis indicated lower selectivity for all the three compounds under galvanostatic conditions when compared to potentiostatic conditions. Both under galvanostatic and potentiostatic conditions, 2-indanone, which exhibits weak adsorption, gave 1-fluoro-2-indanone with high selectivity. 1-Indanone exhibits higher anodic oxidation potential around 2 V. 1,3-Indandione exhibited strong intermediate or product adsorption during voltammetric measurements. The yield and selectivity were much lower for these two compounds under galvanostatic conditions. Quite interestingly in both these cases, the selectivity close to 70% for the monofluorinated compound could be achieved under potentiostatic conditions by passing up to 6 F/mole of electric charge. Prevention of formation of over oxidation products under potentiostatic conditions may be the main cause for this improvement as suggested by chronoamperometric measurements.

1. Introduction

Substituted indanones or carbonyl cyclic derivatives like phenylbutazone and sulfinpyrazone are frequently used analgestic and antipyretic drugs [1]. It is also well known that α-fluoro carbonyl compounds can substantially improve the biological activity of the parent drug molecule [2,3]. There are only few reports on the halogenation of indanones including fluorination either by chemical or electrochemical methods in the literature [1,4]. Substituted 1,3-indandione [1] as well as substituted 1-indanone [4] have been chemically fluorinated using active organic fluorinating agents. 1-Indanone and 2-indanone have also been chemically fluorinated using inorganic fluorinating agents, namely XeF_2 and $CsSO_4F$ [5]. Brief reports on chemical [6] as well as electrochemical fluorination [7] of tetralone are also available.

The main objective of the present work was to study the electrochemical fluorination of 1-indanone, 2-indanone and 1,3-indandione. Solvent free $Et_3N \cdot nHF$ and $Et_4NF \cdot mHF$ were chosen as the electrolyte media due to its utility for fluorinating organic compounds with relatively high oxidation potential [8,9]. Hence $Et_3N \cdot 4HF$ was employed as the electrolyte in the present work. Since, it has been shown earlier that potentiostatic approach gives better selectivity in such compounds which posses relatively high oxidation potential, both potentiostatic and galvanostatic methods were evaluated [10]. Since Pt electrodes exhibited lower anodic limit, cyclic voltammteric measurements are reported in Pt as well as glassy carbon electrodes. In the earlier investigations, it was noticed that even on a Pt electrode, constant potential electrolysis needs to be carried out at a potential which is substantially higher than the oxidation peak potential observed on glassy carbon electrode [10]. To understand this observation, some chronoamperometric investigations on Pt electrodes in the absence and in presence of reactant molecule were also carried out. Some interesting correlation also seems to exist between the nature of adsorption as revealed by cyclic voltammetry and product distribution and selectivity during electrochemical fluorination. These aspects are discussed in detail in this work.

2. Experimental

2.1. Materials

Synthetic grade (>98%) 2-indanone, 1-indanone and 1,3-indandione were purchased from Acros and used without further

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doi:10.1016/j.jelechem.2009.10.023

purification. Triethylamine (>99%) was purchased from Sisco Research Laboratory, India and employed without further purification. Anhydrous hydrogen fluoride (AHF) > 99.9% was obtained from M/s TANFAC, Cudalore, Tamilnadu, India. Preparation of $Et_3N \cdot 4HF$ has been reported elsewhere [11].

2.2. Cyclic voltammetry

Cyclic voltammetry was carried out using an undivided polypropylene cell. The working electrodes were glassy carbon ($0.07\ cm^2$) and platinum ($0.07\ cm^2$). The counter electrode was a smooth platinum foil ($1\ cm^2$) and the reference electrode was a palladium wire. Prior to the experiments, the glassy carbon electrode was polished with 4/0 emery sheet and alumina gel (0.05 μm) and washed with distilled water. Further, the electrode was sonicated for 5 min to remove any adsorbed alumina particles. $Et_3N \cdot 4HF$ was pre-electrolysed at a constant cell voltage of 2.5 V under nitrogen atmosphere to remove moisture and deaerated for 15 min with nitrogen gas to eliminate interfering oxygen before the start of the experiment.

2.3. Chronoamperometry

Chronoamperometry was carried out using an undivided polypropylene cell. The working and counter electrodes were smooth platinum foil ($1 \times 3\ cm^2$) and the reference electrode was a palladium wire.

2.4. Electrochemical fluorination

Undivided polypropylene tube (5 ml) was served as a preparative cell for the anodic fluorination of 2-indanone (**1a**), 1-indanone (**2a**) and 1,3-indandione (**3a**) (for both galvanostatic and potentiostatic electrolysis). The anode and cathode were a rectangular platinum foil ($1 \times 3\ cm^2$) for carrying out galvanostatic electrolysis. Potentiostatic electrolysis was carried out by the same platinum foil ($1 \times 3\ cm^2$) as working and counter electrodes and palladium wire was used as reference electrode. Pre-electrolysis of 5 ml of $Et_3N \cdot 4HF$ solution was carried out at a constant cell voltage of 2.5 V under nitrogen atmosphere. The corresponding current density was around $1.5\ mA/cm^2$ at the start of pre-electrolysis and dropped to 20% of its initial value ($0.3\ mA/cm^2$) after 90 min. The reactant (2-indanone, 1-indanone and 1,3-indanedione, 0.3 mol) was added subsequently and the electrolysis was carried out galvanostatically using an in-house fabricated galvanostat and potentiostatically by BAS IM6 Electrochemical Analyser (USA) at 25 ± 2 °C. After completion of electrolysis, the electrolyte was mixed with 50 ml of cold water and extracted using diethyl ether. The extract was washed with brine solution and dried over anhydrous magnesium sulfate. The ether was distilled and the products were characterized using ^1H NMR, ^{19}F NMR and GC/MS.

2.5. Equipments

The purity of the reactant samples was checked by HPLC (Shimadzu 10VP) with ODS column using UV–Visible detector (254 nm). Methanol–water mixture (70:30) was used as eluent. ^1H NMR spectra were recorded with 400 MHz Bruker NMR Spectrometer with $CDCl_3$ and TMS as solvent and reference respectively. ^{19}F NMR (376.5 MHz) of the products was recorded using $CFCl_3$ as internal reference. The products dissolved in methanol were subjected to GC/MS analysis using Agilent 5975C GC/MSD with Triple-Axis HED-EM detector and 7890A GC. Cyclic voltammetry, potentiostatic and chronoamperometric studies were carried out using BAS IM6 Electrochemical Analyser (USA) and Thales 3.18-USB software.

3. Results and discussion

3.1. Cyclic voltammetry

Selective electrochemical fluorination (SEF) is conveniently carried out using platinum anodes in different fluoride media such as $Et_3N \cdot nHF$ and $Et_4NF \cdot mHF$ [11–16]. However, in $Et_3N \cdot 4HF$ medium, the background current on platinum anode increases sharply above 1.5 V itself (Fig. 1, curve a). This is probably due to catalytic oxidation of trace level organic impurities or even traces quantities of free bases. Preliminary voltammetric measurements on platinum electrodes did not indicate any distinct oxidation peak for all the three compounds (**1a**, **2a** and **3a**) reported here.

Glassy carbon exhibits much lower background current and higher anodic limit in $Et_3N \cdot 4HF$ medium (Fig. 1, curve b). The voltammetric peaks during anodic oxidation of indanones are more clearly observed on glassy carbon electrodes. Hence in the present study, the voltammetric behaviour of indanones are reported on glassy carbon electrodes, while the preparative studies are reported using the conventional platinum anodes and cathodes. Similar approach was also adopted earlier during the SEF of *N*-alkyl and *N*,*N* dialkyl phenylacetamides [10].

Typical cyclic voltammograms of 20, 40, 60 and 80 mM of 2-indanone (**1a**) at a constant sweep rate of 20 mV/s on glassy carbon electrode is shown in Fig. 2A. These voltammograms give a sharp well defined anodic peak at 1.85 V. The anodic peak however, falls sharply beyond the anodic peak potential region without a conventional diffusion tail, suggesting that the process involves weak adsorption step. The anodic peak current for 20 mM of **1a** is quite high. With further additions of 20 mM concentrations, the relative increase in anodic peak current is very low (Fig. 2A, curves b–d). In multi-sweep cyclic voltammogram, the anodic peak currents in the second and subsequent peaks are much smaller than the first anodic peak current value (Fig. 2B, curves b–d). All these observations suggest that, 2-indanone is weakly adsorbed on the anode surface [17–19]. It has been established that the oxidation potential of the weakly adsorbed organic molecule almost coincides with the oxidation potential of the same molecule reaching the electrode surface through diffusion process [17–19]. Both the diffused and weakly adsorbed **1a** species undergo electro-oxidation in the same anodic peak potential region. In an earlier study from this laboratory, it was reported that such weak adsorption of phenyl thioacetates was found to be favourable for achieving higher yield and

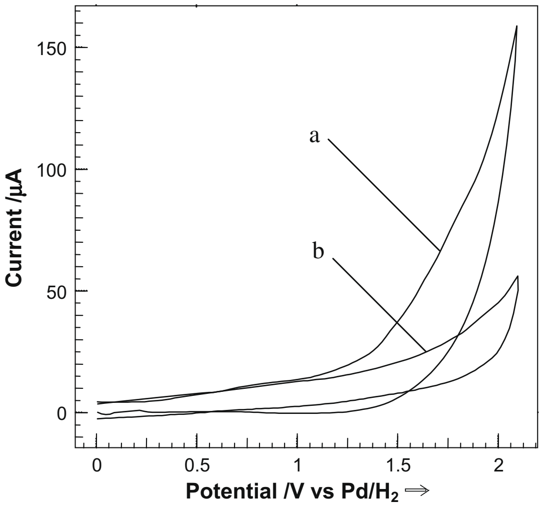


Fig. 1. Cyclic voltammogram for a platinum electrode in neat $Et_3N \cdot 4HF$ (a), **c**yclic voltammogram for a GC electrode in neat $Et_3N \cdot 4HF$ (b).

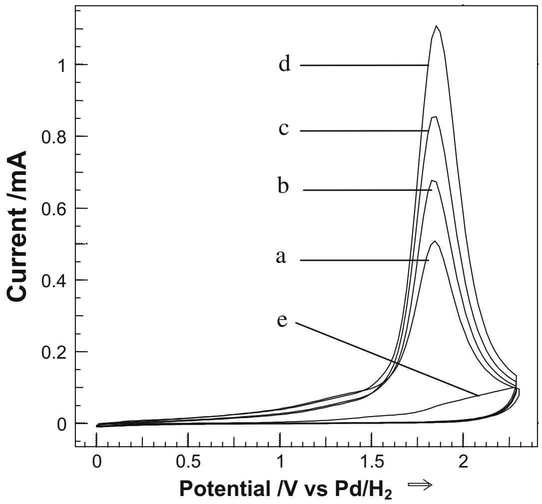


Fig. 2A. Cyclic voltammograms for a glassy carbon electrode in $Et_3N \cdot 4HF$ containing 20 (a), 40 (b), 60 (c), 80 (d) and 0 (e) mM of **1a**. Scan rate 20 mV/s.

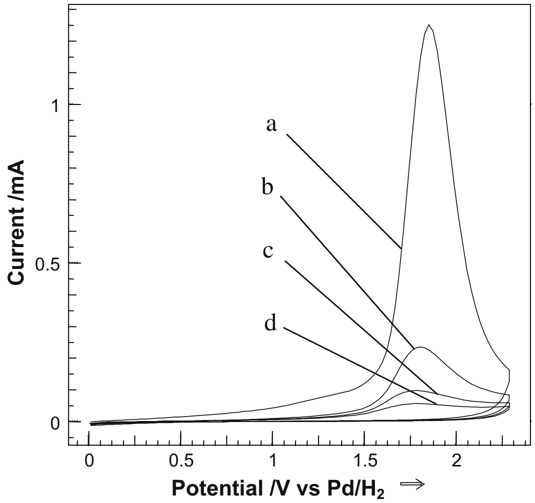


Fig. 2B. Multi sweep for a glassy carbon electrode in $Et_3N \cdot 4HF$ containing 60 mM of **1a**. Scan rate 20 mV/s.

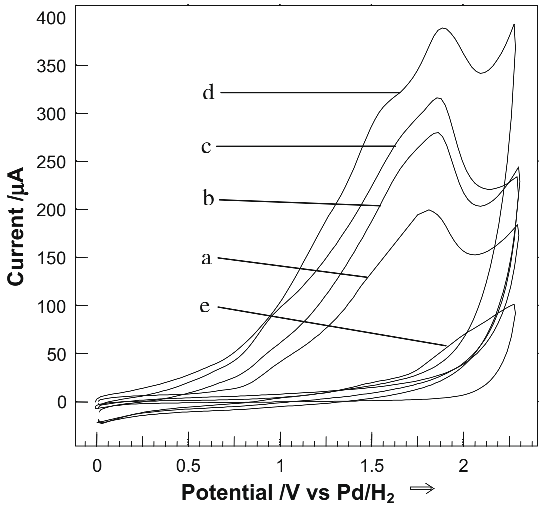


Fig. 3A. Cyclic voltammograms for a glassy carbon electrode in $Et_3N \cdot 4HF$ containing 20 (a), 40 (b), 60 (c), 80 (d) and 0 (e) mM of **3a**. Scan rate 20 mV/s.

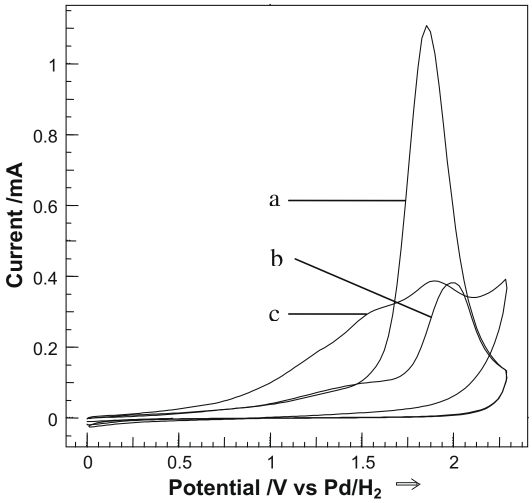


Fig. 3B. Cyclic voltammograms for a glassy carbon electrode in $Et_3N \cdot 4HF$ containing 80 mM of **1a** (a), **2a** (b) and **3a** (c). Scan rate 20 mV/s.

selectivity in electrochemical fluorination [20]. The present study also confirms this view (Section 3.3).

Typical cyclic voltammograms of 20, 40, 60 and 80 mM of 1,3-indandione (**3a**) on glassy carbon electrode at the same sweep rate of 20 mV/s are shown in Fig. 3A. The anodic oxidation in presence of **3a** starts well below 1.5 V, although the main oxidation peak is observed only around 1.8 V. The multi-sweep experiments also indicated substantially lower currents below 1.5 V in the second and subsequent experiments. These observations indicate strong product adsorption following electron-transfer below 1.5 V, which is responsible for the anodic current in the lower potential region. Similar voltammetric responses with separate anodic peak for strong product adsorption have been predicted by Wopschall and Shain [17–19]. The broad first anodic peak (below 1.5 V) is due to this adsorption process accompanied by electrochemical oxidation. The second anodic peak (1.8 V) at more positive potential is apparently due to anodic oxidation of diffused reactant from the bulk solution. Such strong adsorption of reactant, intermediate or product may lead to fouling of the electrode surface and lower selectivity during electrochemical fluorination. It is noted that weak reactant adsorption exhibited by **1a** would assist oxidative fluorination (Fig. 2A), where as strong intermediate adsorption exhibited by **3a** would inhibit the above process (Fig. 3A).

A single irreversible predominantly diffusion controlled wave was obtained for 1-indanone (**2a**) (Fig. 3B, curve b). The oxidation peak potential for this compound is noticed at around 2.05 V suggesting that this is the compound with the highest oxidation potential among the three investigated here. A comparison of the voltammetric responses of 80 mM concentration of all the three compounds in the same medium is shown in Fig. 3B. The anodic peak current is much higher for the weakly adsorbed **1a** (Fig. 3B, curve a). The oxidation process itself starts at much lower potentials suggesting product or intermediate adsorption for **3a** on the electrode surface (Fig. 3B, curve c).

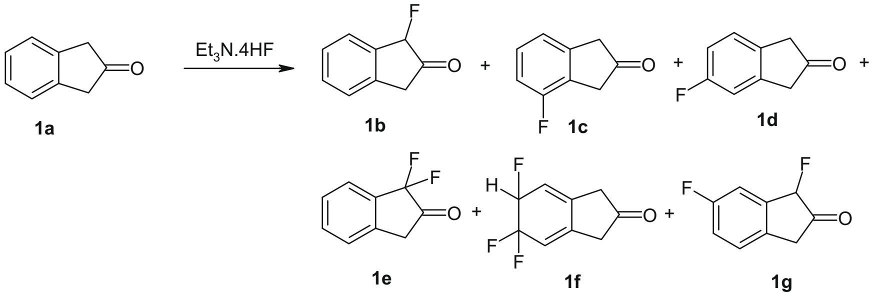
3.2. Selective electrochemical fluorination of 2-indanone

Product analysis from HPLC after galvanostatic electrolysis of 2-indanone (**1a**) (15 mA/cm^2, 2 F/mole) indicated a satisfactory conversion of 68.5% (Table 1, run 2). ^{19}F NMR analysis of extracted product mixture indicated that 1-fluoro-2-indanone (**1b**) was the

Table 1
Effect of current density on SEF of 2-indanone.

Run	Current density (mA/cm^2)	Selectivity[a] (mole%)							
		1b	**1c**	**1d**	**1e**	**1f**	**1g**	Others	Reactant
1	10	48.5	2.3	<1	1.5	<1	<1	13.2	31.5
2	15	66.4	3.3	<1	3.1	1.9	<1	9.2	14.1
3	20	59.2	3.1	1.3	3.9	2.5	1.9	18.3	9.8

Cell voltage = 2.84–3.02 V.
Concentration = 300 mM.
[a] Based on ^{19}F NMR data.



Scheme 1. Selective electrochemical fluorination of 2-indanone.

main product with selectivity close to 49%. A few other fluorinated products with very low yield could also be detected by ^{19}F NMR (Scheme 1). ^{19}F NMR signals for fluorinated products **1b–g** are summarized in Table 2. At least one monofluoro derivative **1b** and one difluoro derivative **1e** could also be confirmed from the GC/MS data (Table 3).

A few experiments were conducted to study the effect of current density on the selective electrochemical fluorination of 2-indanone. This data collected at 10, 15 and 20 mA/cm^2 are summarized in Table 1. Maximum selectivity was obtained at the current density of 15 mA/cm^2 (Table 1, run 2). Although more reactant is consumed at higher current density, the selectivity for the main product **1b** decreases (Table 1).

Under galvanostatic conditions, increasing the electricity to 4 F/mole also lead to poorer selectivity (Table 4, runs 1 and 2). During galvanostatic electrolysis, the overall cell voltage varied between 2.80 and 3.05 V, throughout the electrolysis. However, the selectivity of 1-fluoro-2-indanone improved slightly under potentiostatic conditions (Table 4, runs 3 and 4). Under optimum conditions, (Table 4, run 4) an overall selectivity of 70% can be achieved for the synthesis of 1-fluoro-2-indanone (**1b**) by the constant potential electrolysis from 2-indanone.

Table 2
^{19}F NMR signal of 2-indanone (**1b–g**), 1-indanone (**2b–h**) and 1,3-indandione (**3b–f**).

Compound	1	2	3
b	−177.47 (1F, d) 5.51 (d, 1 H) J_{HF} = 56.5 Hz	−168.59 (1F, d) 5.75 (d, 1H) J_{HF} = 49.7 Hz	−153.54 (1F, br) 6.33 (d, 1H) J_{HF} = 46.4 Hz
c	−114.74 (1F, m)	−194.65 (1F, d) J_{HF} = 49.7 Hz	−116.81 (1F, m)
d	−108.21 (1F, m)	−124.44 (1F, m)	−111.96 (1F, m)
e	−101.58 (2F, s)	−120.59 (1F, m)	−99.40 (2F, s)
f	−193.69 (1F, d) J_{HF} = 56.5 Hz −114.82, −114.15 (2F, m) J_{AB} = 252.2 Hz	−114.21 (1F, m)	−151.68 (1F, br) −115.95 (1F, m)
g	−178.87 (1F, d) J_{HF} = 52.7 Hz −111.35 (1F, m)	−101.72 (2F, s)	
h		−210.89 (1F, d) J_{HF} = 49.7 Hz −115.11 (1F, m)	

3.3. Selective electrochemical fluorination of 1-indanone and 1,3-indanedione

Selective electrochemical fluorination of 1-indanone (**2a**) under galvanostatic conditions were carried out at constant current density of 15 mA/cm^2. The results summarized in Table 5 indicate that around 40% of the starting material remains unreacted after passing 2 F/mole of electric charge. The selectivity of main product 3-fluoro-1-indanone (compound **2b** in Scheme 2) was also low (38%, Table 5, Run 2). Under galvanostatic conditions, even after passing 6 F/mole of charge, the product selectivity did not improve beyond 43% (Table 5, run 3). By increasing electric charge, significant quantity of 2-fluoro-1-indanone (compound **2c**, Scheme 2) was also obtained. These and other minor fluorinated products shown in Scheme 2 were identified by ^{19}F NMR signals (Table 2, compounds **2b–h**). At least three monofluoro derivatives (**2b–d**) and two difluoro derivatives (**2g** and **2h**) could be further confirmed by their fragmentation patterns in GC/MS (Table 3). Differentiating compounds like **2d–f** with monofluoro aromatic ring segments by their GC/MS fragmentation patterns would indeed be difficult.

Compounds such as 1-indanone (**2a**) with high oxidation potentials, can still be selectively fluorinated on platinum electrode under potentiostatic conditions (Table 5, run 4). The conversion as well as the product selectivity could be improved further by increasing the total electric charge passed to 6 F/mole (Table 5, runs 3 and 6). Under potentiostatic conditions further oxidation of organic cation radical intermediate is substantially reduced leading to higher selectivity. The formation of difluoro derivative and other side products is substantially minimized. Under opti-

Table 3
GC/MS data of fluorinated products obtained during anodic fluorination of **1a, 2a** and **3a**.

Compound	GC/MS: m/z:
1b	150 ($[M]^{\cdot+}$, C_9H_7FO, 35.1%); 134 ($[M{-}O]^{\cdot+}$, C_9H_7F, 1.8%); 131 ($[M{-}F]^{+}$, C_9H_7O, 4.5%); 108 ($[C_7H_5F]^{\cdot+}$, 17.5%); 98 ($[C_5H_3FO]^{\cdot+}$, 3.6%); 76 ($[C_6H_4]^{\cdot+}$, 9.0%); 32 ($[CHF]^{\cdot+}$, 100%)
1e	168 ($[M]^{\cdot+}$, $C_9H_6F_2O$, 23.5%); 152 ($[M{-}O]^{\cdot+}$, $C_9H_6F_2$, 14.5%); 149 ($[M{-}F]^{+}$, C_9H_6FO, 13.0%); 130 ($[M{-}F_2]^{\cdot+}$, C_9H_6O, 19.7%); 126 ($[C_7H_4F_2]^{\cdot+}$, 87.9%); 116 ($[C_5H_2F_2O]^{\cdot+}$, 7.3%); 78 ($[C_2F_2O]^{\cdot+}$, 34.8%); 76 ($[C_6H_4]^{\cdot+}$, 28.8%); 50 ($[CF_2]^{\cdot+}$, 100.0%)
2b	150 ($[M]^{\cdot+}$, C_9H_7FO, 100%); 134 ($[M{-}O]^{\cdot+}$, C_9H_7F, 8.2%); 131 ($[M{-}F]^{+}$, C_9H_7O, 26.6%); 122 ($[M\text{-}CO]^{\cdot+}$, C_8H_7F, 78.5%); 98 ($[C_5H_3FO]^{+}$, 9.8%); 76 ($[C_6H_4]^{\cdot+}$, 55.7%); 42 ($[C_2H_2O]^{\cdot+}$, 9.8%); 32 ($[CHF]^{\cdot+}$, 57.3%)
2c	150 ($[M]^{\cdot+}$, C_9H_7FO, 81%); 136 ($[M{-}CH_2]^{\cdot+}$, C_8H_5FO, 4.1%); 134 ($[M{-}O]^{\cdot+}$, C_9H_7F, 8.2%); 131 ($[M{-}F]^{+}$, C_9H_7O, 26.6%); 122 ($[M{-}CO]^{\cdot+}$, C_8H_7F, 100%); 104 ($[C_7H_4O]^{\cdot+}$, 24.5%); 98 ($[C_5H_3FO]^{+}$, 9.8%); 76 ($[C_6H_4]^{\cdot+}$, 55.7%); 60 ($[C_2HFO]^{\cdot+}$, 12.3%); 32 ($[CHF]^{\cdot+}$, 58.3%);
2d	150 ($[M]^{\cdot+}$, C_9H_7FO, 100%); 134 ($[M{-}O]^{\cdot+}$, C_9H_7F, 8.2%); 131 ($[M{-}F]^{\cdot+}$, C_9H_7O, 26.6%); 122 ($[M{-}CO]^{\cdot+}$, C_8H_7F, 78.5%); 94 ($[C_6H_3F]^{\cdot+}$, 35.2%); 80 ($[C_5H_4O]^{\cdot+}$, 4.1%); 31 ($[CF]^{+}$, 68.9%)
2g	168 ($[M]^{+}$, $C_9H_6F_2O$, 100%); 152 ($[M{-}O]^{\cdot+}$, $C_9H_6F_2$, 3.0%); 149 ($[M{-}F]^{\cdot+}$, C_9H_6FO, 66.0%); 140 ($[M{-}CO]^{\cdot+}$, $C_8H_6F_2$, 20.0%); 130 ($[M{-}F_2]^{\cdot+}$, C_9H_6O, 80%); 118 ($[M{-}CF_2]^{\cdot+}$, $[C_8H_6O]^{\cdot+}$, 10.0%); 116 ($[C_5H_2F_2O]^{\cdot+}$, 3.0%); 76 ($[C_6H_4]^{\cdot+}$, 68.0%); 50 ($[CF_2]^{\cdot+}$, 70.0%)
2h	168 ($[M]^{+}$, $C_9H_6F_2O$, 55.0%); 152 ($[M{-}O]^{\cdot+}$, $C_9H_6F_2$, 2.5%); 149 ($[M{-}F]^{+}$, C_9H_6FO, 21.0%); 133 ($[M{-}FO]^{+}$, C_9H_6F, 22.0%); 130 ($[M{-}F_2]^{\cdot+}$, C_9H_6O, 89.0%); 126 ($[C_7H_4F_2]^{\cdot+}$, 3.7%); 98 ($[C_5H_3FO]^{\cdot+}$, 10.0%); 94 ($[C_6H_3F]^{\cdot+}$, 35.6%); 32 ($[CHF]^{\cdot+}$, 100%); 31 ($[CF]^{+}$, 68.0%)
3b	164 ($[M]^{\cdot+}$, $C_9H_5FO_2$, 100%); 148 ($[M{-}O]^{\cdot+}$, C_9H_5FO, 12.3%); 145 ($[M{-}F]^{+}$, $C_9H_5O_2$, 1.8%); 112 ($[C_5HFO_2]^{+}$, 9.6%); 104 ($[C_7H_4O]^{\cdot+}$, 14.9%); 76 ($[C_6H_4]^{\cdot+}$, 12.2%); 32 ($[CHF]^{\cdot+}$, 78.5%)
3c	164 ($[M]^{\cdot+}$, $C_9H_5FO_2$, 100%); 148 ($[M{-}O]^{\cdot+}$, C_9H_5FO, 17.0%); 145 ($[M{-}F]^{+}$, $C_9H_5O_2$, 3.5%); 133 ($[C_8H_5O_2]^{+}$, 34.0%); 125 ($[C_6H_2FO_2]^{+}$, 11.0%); 94 ($[C_5H_2O_2]^{\cdot+}$, 42.0%); 57 ($[C_3H_2F]^{+}$, 30.0%); 31 ($[CF]^{+}$, 80.0%)
3e	182 ($[M]^{\cdot+}$, $C_9H_4F_2O_2$, 20.9%); 166 ($[M{-}O]^{\cdot+}$, $C_9H_4F_2O$, 2.6%); 163 ($[M{-}F]^{+}$, $C_9H_4O_2F$, 100%); 144 ($[M{-}F_2]^{\cdot+}$, $[C_9H_4O_2]^{+}$, 14.6%); 130 ($[C_5F_2O_2]^{\cdot+}$, 4.8%); 104 ($[C_7H_4O]^{\cdot+}$, 48.5%); 78 ($[C_2F_2O]^{\cdot+}$, 11.7%); 76 ($[C_6H_4]^{\cdot+}$, 58.3%); 50 ($[CF_2]^{\cdot+}$, 48.5%)
3f	182 ($[M]^{\cdot+}$, $C_9H_4F_2O_2$, 14.6%); 166 ($[M{-}O]^{\cdot+}$, $C_9H_4F_2O$, 2.0%); 163 ($[M{-}F]^{+}$, $C_9H_4O_2F$, 37.7%); 154 ($[M{-}CO]^{\cdot+}$, $C_8H_4F_2O$, 4.1%); 147 ($[C_9H_4FO]^{+}$, 10.3%); 122 ($[C_7H_3FO]^{\cdot+}$, 60.7%); 112 ($[C_5HFO_2]^{\cdot+}$, 16.4%); 94 ($[C_6H_3F]^{\cdot+}$, 100%); 57 ($[C_3H_2F]^{+}$, 15.9%); 32 ($[CHF]^{\cdot+}$, 47.5%); 31 ($[CF]^{+}$, 61.5%)

Table 4
SEF of 2-indanone. Effect of electrolysis method and electric charge.

Run Type		Charge (F/mole)	Selectivity[c] (mole%)							
			1b	**1c**	**1d**	**1e**	**1f**	**1g**	Others	Reactant
1	Galvanostatic[a]	2	66.4	3.3	<1	3.1	1.9	<1	9.2	14.1
2		4	57.6	4.9	1.4	11.7	2.6	3.1	11.3	7.4
3	Potentiostatic[b]	2	69.7	<1	<1	10.3	–	–	7.9	10.1
4		4	72.3	1.3	<1	12.3	–	–	8.3	4.8

Concentration = 300 mM.

[a] Current density = 15 mA/cm^2; cell voltage = 2.84–2.91 V.

[b] Potential = 2.15 V.

[c] Based on ^{19}F NMR data.

Table 5
SEF of 1-indanone. Effect of electrolysis method and electric charge.

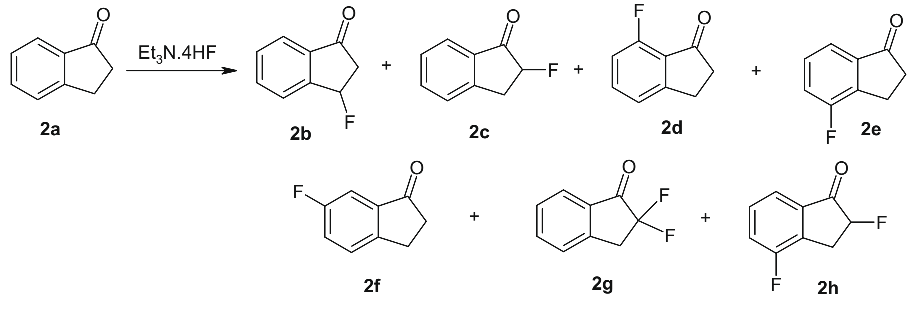
Run Type		Charge (F/mole)	Selectivity[c] (mole%)								
			2b	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	Others	Reactant
1	Galvanostatic[a]	2	38.3	7.3	2.1	<1	<1	4.4	2.1	3.1	40.7
2		4	42.2	10.5	3.2	1.5	1.3	10.3	2.3	4.4	24.3
3		6	43.3	16.2	4.1	1.7	1.9	16.1	3.4	5.1	8.2
4	Potentiostatic[b]	2	49.5	4.5	–	–	2.6	–	–	4.5	38.9
5		4	63.5	6.7	–	–	5.2	–	–	6.1	18.5
6		6	69.8	7.3	–	–	12.3	–	–	5.9	4.7

Concentration = 300 mM.

[a] Current density = 15 mA/cm^2; cell voltage = 2.89–2.98 V.

[b] Potential = 2.3 V.

[c] Based on ^{19}F NMR data.



Scheme 2. Selective electrochemical fluorination of 1-indanone.

Table 6
SEF of 1,3-indandione. Effect of electrolysis method and electric charge.

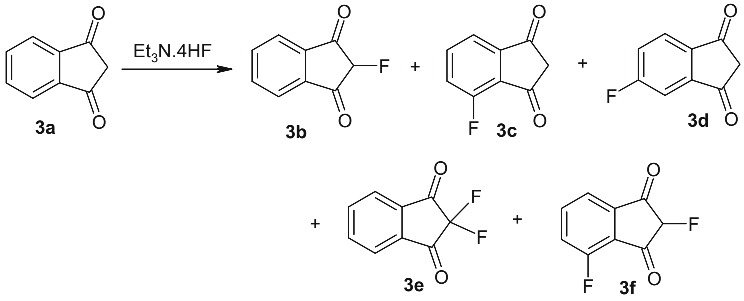
Run Type		Charge (F/mole)	Selectivity[c] (mole%)						
			3b	**3c**	**3d**	**3e**	**3f**	Others	Reactant
1	Galvanostatic[a]	2	38.4	1.5	1.3	4.4	<1	4.1	49.3
2		4	46.9	3.8	2.9	5.9	1.2	10.0	29.3
3		6	51.6	5.1	3.4	9.5	1.7	12.1	16.6
4		8	42.1	6.7	3.5	19.1	2.5	15.4	10.7
5	Potentiostatic[b]	2	45.7	5.6	<1	2.6	–	6.2	38.9
6		4	57.2	7.4	1.6	4.2	–	8.1	21.5
7		6	69.7	11.1	3.2	5.1	–	6.2	4.7

Concentration = 300 mM.

[a] Current density = 15 mA/cm^2; cell voltage = 2.95–3.05 V.

[b] Potential = 2.4 V.

[c] Based on ^{19}F NMR data.



Scheme 3. Selective electrochemical fluorination of 1,3-indandione.

mum conditions, the selectivity of 3-fluoro-1-indanone (**2b**) could be improved to 70% (Table 5, run 6).

The voltammetric investigations showed that 1,3-indandione (**3a**) can be easily oxidized electrochemically even below 1 V (Fig. 3A). However, under galvanostatic conditions, this compound showed poor conversion and selectivity (Table 6, runs 1–4). By consumption of 2 F/mole of electric charge, almost 50% of the starting material remained unreacted (Table 6, run 1). With further increase of electric charge (6 F/mole), a selectivity of 50% for the main product 2-fluoro-1,3-indandione (compound **3b**, Scheme 3) could be achieved (Table 6, run 3). There is no improvement in the selectivity by further increasing the electric charge (Table 6, run 4). In addition to the main product (**3b** in Scheme 3) at least four other fluorinated products could be identified by ^{19}F NMR (Table 2). At least two monofluoro derivatives (**3b** and **3c**) and two difluoro derivatives (**3e** and **3f**) could also be further confirmed by their fragmentation pattern obtained by GC/MS.

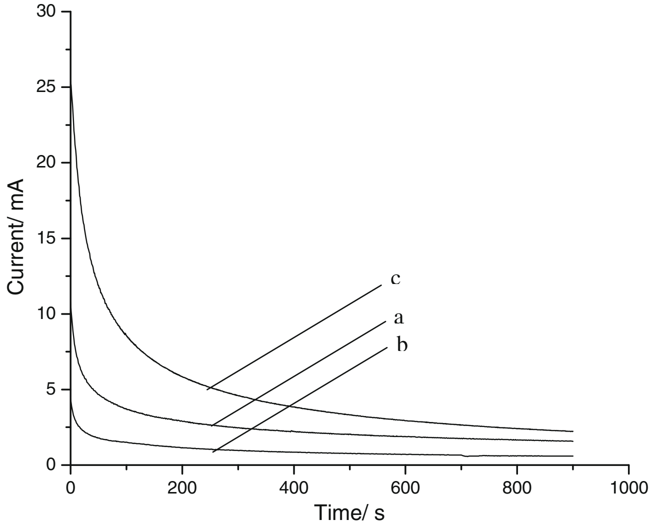


Fig. 4A. Chronoamperometric curves recorded at 2.0 V for initial period of 15 min before pre-electrolysis (a), after pre-electrolysis (b) and 0.3 M of 2-indanone (c).

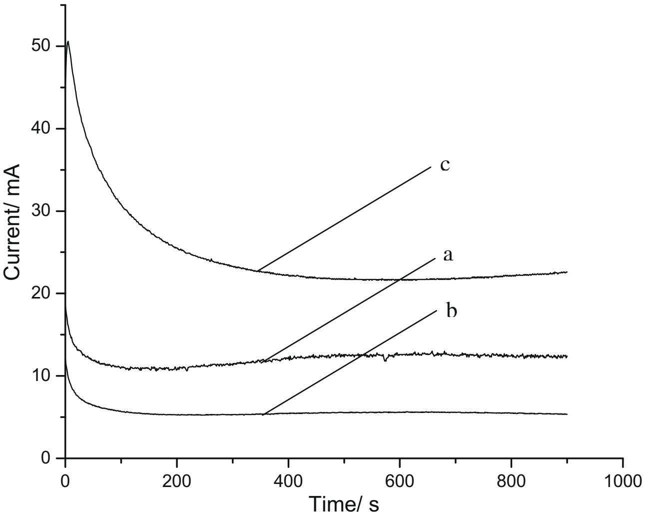


Fig. 4B. Chronoamperometric curves recorded at 2.2 V for initial period of 15 min (a) before pre-electrolysis (a), after pre-electrolysis (b) and 0.3 M of 2-indanone (c).

Quite interestingly, this compound also showed improved selectivity during selective electrochemical fluorination under potentiostatic conditions (Table 6, runs 5–7). The conversion and selectivity could be improved by passing 6 F/mole of electric charge.

Under optimum conditions, once again around 70% selectivity for 2-fluoro-1,3-indandione (**3b**) could be achieved.

3.4. Chronoamperometry

Some chronoamperometric measurements were also carried out to understand the cause for improved selectivity under potentiostatic conditions on Pt electrodes in the case of indanones reported above and alkyl phenylacetamides reported earlier [8].

The chronoamperometric curves recorded at 2.0 V in $Et_3N \cdot 4HF$ medium before pre-electrolysis, after pre-electrolysis at 2.0 V for 2 h and after addition of 2-indanone for the initial period of 15 min are presented in Fig. 4A, curves a–c respectively. In all the three cases, a systematic decrease in current with time is noticed. After pre-electrolysis the current at 15 min for example is found to decrease from 1.57 mA (Fig. 4A, curve a) to 0.59 mA (Fig. 4A, curve b). At this voltage (2.0 V) even after addition of 0.3 M 2-indanone, the anodic current after 15 min was found to increase only slightly to 2.23 mA (Fig. 4A, curve c). Though the applied potential (2.0 V) is higher than the anodic peak potential for this compound, (1.85 V) the oxidation current does not increase significantly.

The chronoamperometric responses obtained for the same cases a–c shown inFig. 4A, at a higher anodic potential of 2.2 V are shown in Fig. 4B. The current observed before pre-electrolysis after 15 min is substantially higher at 12.37 mA (Fig. 4B, curve a). Even after pre-electrolysis under identical conditions at 2.2 V, the cell current was found to be significantly higher at 5.35 mA (Fig. 4B, curve b). In presence of 2-indanone, the oxidation current was as high as 22.50 mA at 2.2 V (Fig. 4B, curve c).

It appears that a small concentration of the free base triethylamine is always present in the electrolyte $Et_3N \cdot 4HF$ (Eq. (1)).

$$Et_3NH \cdot H_2F_3 + HF \leftrightharpoons Et_3N + 4HF \qquad (1)$$

The free base can undergo electrochemical oxidation on Pt electrode leading to cation radical formation and further anodic coupling processes leading to film formation on the electrode surface. It should be noted that a thin easily removable film is always noticed on Pt anode surface after electrolysis in the absence or in presence of reactant molecules, both during galvanostatic and potentiostatic electrolysis. The rising portion of the chronoamperometric curves obtained at 2.2 V both before and after pre-electrolysis may be attributed to this oxidative film formation (Fig. 4B, curves a and b). Even in presence of organic compound, this rising trend is noticed after some more time delay (Fig. 4B, curve c).

$$Et_3N - 1e^- \leftrightharpoons R_3N^+ \qquad (2)$$

It appears that reaction 2 and the resulting film formation influences the product selectivity under potentiostatic conditions in two ways. The polymeric film provides some resistance to the oxidation of organic compound and hence the constant potential electrolysis proceeds smoothly only at 2.2 V rather than 2.0 V. Secondly, under constant potential conditions, as the reactant concentration decreases, the trialkylamine oxidation preferably occurs and thus prevents over oxidation of the monofluoro derivative. This ensures better selectivity for all the three compounds under galvanostatic conditions.

4. Conclusions

Among the three investigated compounds, 2-indanone undergoes weak reactant adsorption. This compound lead to good conversion and selectivity both under galvanostatic and potentiostatic conditions and gets oxidized only around 2.0 V. In contrast 1-indanone which also has an oxidation peak around this region does not show weak adsorption. 1,3-indandione is oxidized at substantially lower potential, but oxidation appears to be due to strong intermediate or product adsorption. In both these cases, galvanostatic electrolysis leads to over oxidation of the reactant leading to lower selectivity of the desired mono fluorinated products. In such cases constant potential electrolysis appears to be ideal. Although up to 6 F/mole of electric charge is to be passed, the selectivity close to 70% could still be achieved for the fluorination of 1-indanone as well as 1,3-indandione. The excess current in this case appears to be consumed by the oxidation of either impurities or the small equilibrium concentration of trialkyl amine in the electrolyte thus preventing over oxidation of the desired fluorinated product under potentiostatic conditions.

Acknowledgements

The authors wish to thank CSIR, New Delhi for granting SRF and J. Kennedy, CECRI for taking GC/MS spectral data.

References

[1] G. Resnati, D.D. Desmarteau, J. Org. Chem. 57 (1992) 4281–4284.
[2] J. Fried, E.F. Sabo, J. Am. Chem. Soc. 76 (1954) 1455–1456.
[3] S. Rozen, R. Filler, Tetrahedron 41 (1985) 1111–1153.
[4] Y. Takeuchi, T. Suzuki, A. Satoh, T. Shiragami, N. Shibata, J. Org. Chem. 64 (1999) 5708–5711.
[5] S. Stavber, B. Sket, B. Zajc, M. Zupan, Tetrahedron 45 (1989) 6003–6010.
[6] F.A. Davis, W. Han, Tetrahedron Lett. 32 (1991) 1631–1634.
[7] V. Dinoiu, T. Fukuhara, K. Miura, N. Yoneda, J. Fluorine Chem. 121 (2003) 227–231.
[8] T. Fuchigami, T. Tajima, J. Fluorine Chem. 126 (2005) 181–187.
[9] S. Inagi, T. Sawamura, T. Fuchigami, Electrochem. Commun. 10 (2008) 1158–1160.
[10] N. Ilayaraja, M. Noel, J. Electroanal. Chem. 632 (2009) 45–54.
[11] N. Ilayaraja, A. Manivel, D. Velayutham, M. Noel, J. Fluorine Chem. 129 (2008) 185–192.
[12] N. Yoneda, J. Fluorine Chem. 105 (2000) 205–207.
[13] K.M. Dawood, Tetrahedron 60 (2004) 1435–1451.
[14] M. Noel, V. Suryanarayanan, J. Appl. Electrochem. 34 (2004) 357–369.
[15] T. Fuchigami, J. Fluorine Chem. 128 (2007) 311–316.
[16] A. Dinoiu, Rev. Roum. Chim. 52 (2007) 453–466.
[17] R.H. Wopschall, I. Shain, Anal. Chem. 39 (1967) 1514–1527.
[18] R.H. Wopschall, I. Shain, Anal. Chem. 39 (1967) 1527–1534.
[19] R.H. Wopschall, I. Shain, Anal. Chem. 39 (1967) 1535–1542.
[20] V. Suryanarayanan, S. Chellammal, M. Noel, J. Fluorine Chem. 93 (1999) 53–59.