

## PROCESS OPTIMISATION STUDIES ON THE ELECTROCHEMICAL PERFLUORINATION OF HEXANOYL, OCTANOYL AND DECANOYL CHLORIDE

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[Received: 25 October 1996 Accepted: 5 March 1998]

The effect of different operating parameters on the electrochemical perfluorination (ECPF) of octanoyl chloride was studied in detail. The effect of pre-electrolysis time, cell voltage, concentration of the reactant and the time distribution of reactant in the electrolyte and the overall charge passed on the yield and product distribution are presented. The advantages of operating the cell at constant current density within a specified cell voltage range are also highlighted. The optimum operating conditions arrived at for octanoyl chloride was also found to be suitable for the ECPF of hexanoyl and decanoyl chlorides.

**Keywords:** Electrochemical fluorination, octanoyl chloride, hexanoyl and decanoyl chlorides.

### INTRODUCTION

Perfluoro octanoyl fluoride was one of the early products obtained through electrochemical perfluorination (ECPF) route [1-4] which also found extensive commercial applications [5,6]. Efforts towards improving the process by operating at higher cell voltages of the order of 9-12 volts, [7], use of foam nickel anode [8,9], operating at lower cell temperatures [10], circulation of electrolyte [11], optimising the reactant concentration [12], operating the ECPF reactor at constant current [13,14] and use of partially fluorinated starting materials [15] have been reported. There is very little report on the ECPF of hexanoyl and decanoyl chloride [3] in the literature. The present investigation presents a detailed study for ECPF process with the objective of further improving the overall process efficiency.

### EXPERIMENTAL

High purity nickel plates (99.99% MIDHANI, India) were used as anodes as well as cathodes. The electrode pack comprising parallel plates of nickel was kept in a 250 ml capacity stainless steel jacketed cell with provision for cooling. The cell was provided with a discharge valve and the top portion was connected to a condenser. Two separate circulating coolers (JULABO F-55 AND F-10, Germany) were used to control the temperature of cell and condenser. The gaseous uncondensed effluents from the top of

condenser were allowed to pass through a series of traps containing NaF, NaS<sub>2</sub>O<sub>3</sub>-KI mixture and water. The entire set-up was accommodated in a fume chamber with exhaust facility. The perfluorinated product isolated at the end of ECPF was refluxed with potassium hydroxide solution and ether extracted to isolate the perfluoroether from the product mixture. The aqueous layer was treated with concentrated sulphuric acid to recover the perfluoro octanoic acid. Both these fractions were identified by comparing <sup>19</sup>F NMR and IR spectra of these samples with the standard samples (Fluorocarbon, UK).

High purity octanoyl chloride (Aldrich, USA) and liquid AHF (TANFAC, India) were used as such without any further purification.

### RESULTS AND DISCUSSION

#### Electrochemical fluorination of octanoyl chloride

Pre-electrolysis voltage was varied between 5 and 7V. Pre-electrolysis was carried out for the duration of few hours to over 120 hours. Electrochemical fluorination under different conditions of pre-electrolysis indicate that the optimum pre-electrolysis condition is quite close to that reported by Drakesmith et al. The pre-electrolysis is preferably carried out in two stages. In the first stage electrolysis is conducted at a voltage of 5 V until a constant low current density is maintained for 6 hours. The current density during this period drops from 5 mA cm<sup>-2</sup> to about 2 to 2.5 mA cm<sup>-2</sup>. This is

TABLE I: Effect of cell voltage

Cell Voltage for ECF (V)	Yield of perfluorinated products (%)	C.E. (%)	Selectivity* for POA (%)
6.0	53.6	47.2	15.2
6.5	49.3	40.8	18.5
7.0	56.9	50.9	32.6
7.5	47.6	52.6	22.7
8.0	45.2	43.4	18.9
8.5	43.6	44.7	18.5

$$* \text{ Selectivity } \% = \frac{A}{B} \times 100$$

where A = Wt of perfluorinated acid obtained;  
B = Total wt. of perfluorinated product formed.  
POA = Perfluoro octanoic acid

followed by further pre-electrolysis at 5.5 V to achieve a steady current once again for 6 hours. In general pre-electrolysis is completed in about 30 hours and on an average about 30 ampere hour is passed for a 200 ml capacity cell during pre- electrolysis.

After pre-electrolysis, the ECPF of the carboxylic acid is carried out by charging the acid chloride in the cell 4.5 to 5.0% (w/v) octanoyl chloride in the electrolyte was found to yield better results. The electrolysis is initiated with 4.5% reactant concentration. The second and subsequent additions are made when 80-85% of the theoretical charge required has been passed. This also ensures that the cell current at any point of time does not drop below 50% of the initial current.

The optimum cell voltage for electrochemical fluorination initially suggested as 6.0 V was also reexamined in recent works. Total cell voltage upto 12 V has been suggested [7-9]. The yield and selectivity of perfluoro octanoic acid as a percentage of total perfluorinated product yield obtained at different operating cell voltages are summarised in Table I. The total yield and current efficiency of perfluorinated products (acid fluoride and ether) increase with cell voltage

TABLE II: ECF of hexanoyl chloride

Nature of AHF	Cell voltage (V)	Yield of perfluorinated products (%)	C E (%)	Selectivity for perfluorohexanoyl fluoride (%)
Fresh <sup>1</sup>	6.0	27.5	24.7	30.1
Fresh <sup>1</sup>	6.5	44.6	49.5	35.2
Fresh <sup>1</sup>	7.0	57.7	53.4	40.4
Fresh <sup>1</sup>	7.5	50.6	46.2	32.6
Fresh <sup>1</sup>	7.0	51.2	49.9	35.0
Reuse <sup>2</sup>	7.0	52.2	49.6	32.2
Fresh <sup>3</sup>	6-6.5	57.8	62.7	34.8
Fresh <sup>3</sup>	6-6.5	58.3	60.4	40.6

- 1 under constant cell voltage conditions
- 2 fresh expt and reuse
- 3 under constant CD conditions

TABLE III: ECF of decanoyl chloride

Fresh reuse/AHF	Cell voltage (V)	Yield of perfluorinated products (%)	CE (%)	Selectivity for PDA (%)
Fresh <sup>1</sup>	6.5	27.7	34.1	30.5
Fresh <sup>1</sup>	7.0	35.7	40.4	37.6
Fresh <sup>1</sup>	7.5	37.1	46.2	40.0
Fresh <sup>1</sup>	8.0	29.5	36.2	31.4
Fresh <sup>2</sup>	7.0	37.5	45.5	36.5
Reuse <sup>2</sup>	7.0	40.2	55.7	30.1
Reuse <sup>2</sup>	7.0	42.4	50.0	32.2
Fresh <sup>3</sup>	6-6.5	42.6	42.9	37.5
Fresh <sup>3</sup>	6-6.5	40.0	40.8	35.8

- 1 under constant cell voltage
  - 2 fresh and reuse of electrolyte
  - 3 under constant current density
- PDA: Perfluoro decanoic acid

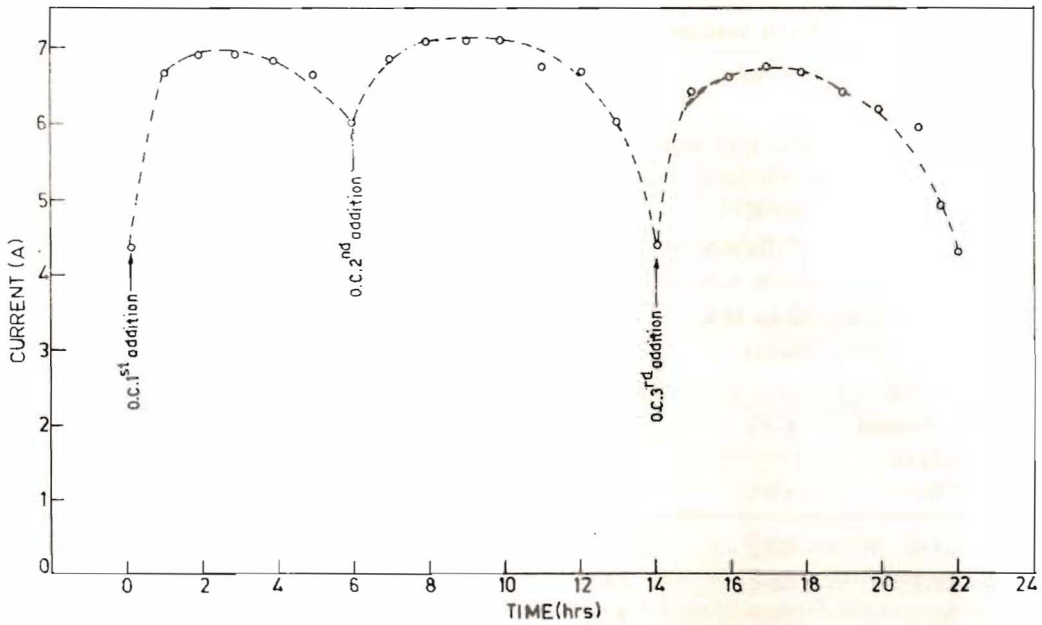


Fig. 1: Current vs time curve for the ECF of octanoyl chloride (OC) at constant cell voltage of 7 V

upto 8 V. But selectivity for undecomposed perfluoro octanoic acid is found to decrease beyond a cell voltage of 7 V. Hence for achieving high selectivity of perfluoro octanoic acid, 7 V is found to be the optimum cell voltage. 283 K is found to be the optimum temperature for the electro-fluorination of octanoyl chloride irrespective of cell voltage employed.

By proper control of experimental parameters for a particular compound, it is indeed possible to achieve a fairly high degree of reproducibility. For example, for experiments

carried out at 7 V gave reproducibility within a range of 5 to 6%.

In these experiments electrode deactivation is noticed whenever the current was allowed a flow at extremely low level (say below 1/3 of the initial current). Typical current-time curve obtained during the electrolysis at constant cell voltage is presented in Fig. 1. From this figure it is apparent that the drop in current is noticed only towards the end of electrolysis or when the reactant concentration decreases significantly. Hence to ensure reproducibility the

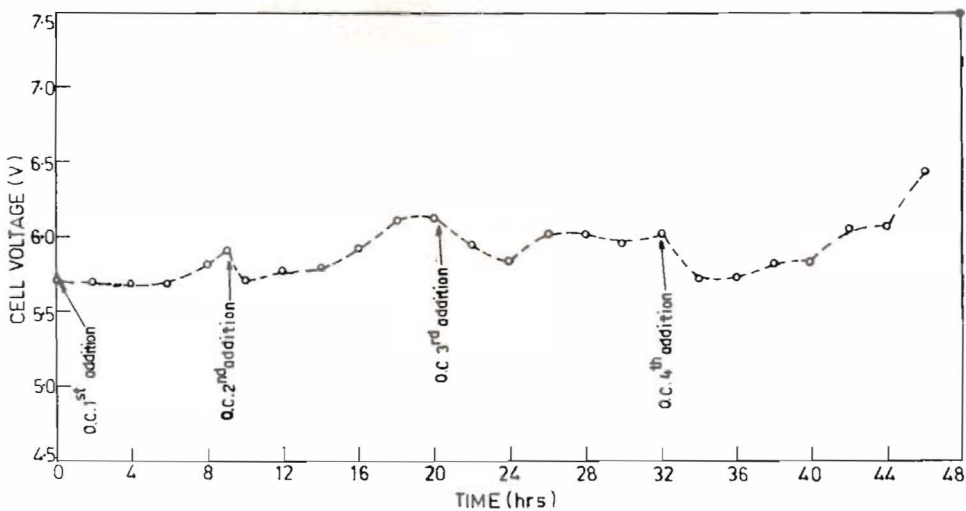


Fig. 2: Cell voltage vs time curve for the ECF of octanoyl chloride (OC) at constant CD of  $18 \text{ mA cm}^{-2}$

reactant concentration was increased or electrolysis stopped when the current drops to 35% of the average current.

Under galvanostatic conditions the cell voltage was found to be remarkably stable at low level of 5.6 to 5.8 V for most part of the electrolysis. The potential-time curve during a typical constant current electrolysis experiment is presented in Fig. 2. Fairly satisfactory current efficiencies above 40% with high selectivity for perfluoro octanoyl fluoride above 35% was obtained in these experiments.

#### Electrochemical fluorination of hexanoyl and decanoyl chloride

The results obtained during the electrochemical fluorination of hexanoyl chloride are summarized in Table IV. Cell voltage once again had significant effect on the yield and current efficiency. Maximum yield, current efficiency and selectivity for perfluoro hexanoic acid was obtained at an operating cell voltage of 7 V (Table II, expt. Nos. 1 to 4). The electrolyte could be effectively reused to achieve further perfluorination (Table II expt. Nos. 5a & b). It was also possible to carry out the electrochemical fluorination under constant current conditions. As in the case of octanoyl chloride the cell voltage remained quite stable throughout the electrolysis and the yield and current efficiency improved marginally.

The results obtained during the ECPF of decanoyl chloride are summarised in Table III. With increase in chain length the yield of perfluorinated acid decreases (Compare Tables I to III). 7.0 to 7.5 V is the optimum cell voltage for this compound as well (Table III expt. Nos. 1 to 4). Even under optimum conditions the maximum yield remain only around 35%. For this compound under constant cell voltage conditions, the current falls sharply when about 80% of the theoretical charge required for perfluorination is passed requiring the electrolysis to be stopped well before the theoretical charge required for ECPF could be passed. The apparent current efficiency is thus higher under these conditions (Table III).

In this case also the electrolyte after isolation of the product could be reused subsequently (Table III, expt. Nos. 5a to c). Electrochemical perfluorination can be carried out at constant current densities as well (Table III, expt. Nos. 6 & 7).

#### CONCLUSION

The following general conclusions regarding the electrofluorination of carboxylic acid chlorides may be drawn from the experimental results presented above.

1. Pre-electrolysis of liquid HF is indeed very important. Film formation and activation of nickel anode seems to be very important during this pre-electrolysis period. A two stage pre- electrolysis at constant cell voltage conditions at 5 V initially and at 5.5 V subsequently

until a steady current for six hours reached is found to be the best.

2. The cell voltage does play an important role in improving the yield and selectivity of electrochemical fluorination (ECF). The actual cell voltage would depend on cell design parameters like interelectrode distance and electrolyte resistance. In the present study 7 V was found to be the optimum for maximum efficiency and selectivity.
3. The cell voltage and the operating current density are directly related to each other. However, it is found to be more convenient to operate the cell at constant current density rather than constant cell voltage. It is however, necessary to ensure that neither the cell voltage increases beyond 7.5 V nor the cell current decreases below 35% of the average current density. This is found to be necessary to ensure good reproducibility and effective reuse of the electrolyte containing partially fluorinated intermediates.
4. It is found that the same operating parameters can be employed for effective perfluorination of hexanoyl, octanoyl and decanoyl chlorides. The total yield and selectivity however decrease with increasing chain length.

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