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THE ELECTROCHEMICAL FLUORINATION OF ACETYL FLUORIDE

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SUMMARY

The electrochemical fluorination of acetyl fluoride in anhydrous hydrogen fluoride to produce trifluoroacetyl fluoride was investigated in a microprocessor-aided modified Simons′ reactor. The product was recovered in acetic acid as trifluoroacetic acid. The experiments were carried out at a controlled anodic potential using a Cu/CuF_2 reference electrode. Product yields of 36 - 45%, current efficiencies of 30 to 50% and energy efficiencies of 11 - 23% were obtained.

Experimental results of this investigation are presented and discussed.

INTRODUCTION

Perfluorocarboxylic acids possess no carbon bound hydrogens and are characterized by a high degree of stability and a relatively low boiling point. Because of the extreme electronegative nature of fluorine, these compounds are strong acids and are completely ionized in water solution [1]. Trifluoroacetic acid is a good solvent for polyesters and proteins and undergoes reactions typical of a carboxyl acid. In addition to its commercial importance, as a simple perfluorocarboxylic acid its synthesis by electrochemical means should provide insight on the whole class of such acids.

The three general methods of replacing hydrogen with fluorine in an organic molecule are reaction with elemental fluorine, reaction with a metal fluoride and electrochemical fluorination. The advantages and disadvantages of each of these methods has been discussed extensively elsewhere and will not be repeated here. Rather, we will focus on the production of trifluoroacetic acid.

The formation of trifluoroacetic acid via electrochemical fluorination was first reported by Simons using acetic acid as a starting material [2]. The resulting product, trifluoroacetyl fluoride, was then hydrolyzed to form trifluoroacetic acid. Scholberg and Brice reported the production of trifluoroacetic acid by electrochemical fluorination using acetyl chloride as the reactant [3]. They stated that the acetyl chloride reacted to form acetyl fluoride upon addition to anhydrous hydrogen fluoride (AHF). Also, conductivity additives were needed in this study as the acetyl fluoride/AHF mixture possessed a very low conductivity. The yields of the product were good, being in excess of 85% based on product recovered.

Electrochemical fluorination processes use relatively inexpensive starting materials and operate at mild experimental conditions resulting in the retention of functional groups. This process is well-suited for the study of synthesizing trifluoroacetic acid or its precursor, since the solubilities of the hydrocarbon reactants used, acetic acid or acetyl fluoride, in anhydrous hydrogen fluoride are very good. However, in the past, electrochemical fluorination studies have been plagued with problems of poor reproducibility, low chemical yields and poor selectivities. Furthermore, applications of electrochemical engineering principles of the process have been limited. Hence, it is believed that using a well-designed and well-controlled electrochemical reactor to investigate the production of trifluoroacetic acid will be helpful in the understanding and enhancement of this electrochemical fluorination process.

EXPERIMENTAL

In this investigation, a modified Simons' type reactor was developed. This reactor design was based on one used in our previous investigation [4]. The criteria of the design and the mass transfer characteristics of the reactor have been described extensively [4].

The version of the reactor used in this study was fabricated from monel and coated with a high temperature FEP teflon coating. Figure 1 shows the top view of the reactor. The total volume of the reactor is ~750 ml. All of the anodes and cathodes were fabricated using 0.159 cm thick nickel 200 sheet, (99.5% nickel.) The total apparent anodic surface area is 216 cm^2 whereas the total cathodic surface area is 432 cm^2. The electrodes were arranged in four monopolar packs of three electrodes each, with the anode sandwiched between two cathodes in each pack. The rest of the stirrer and gas inlets and outlets arrangements in the reactor were identical to those described in the previous studies.

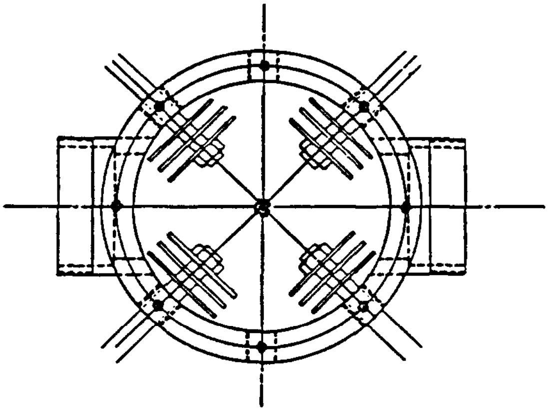

Fig.1. Top View of the Modified Simons' Reactor.

Figure 2 shows the electrochemical fluorination system. This schematic is similar to that used previously except a bank of three product recovery traps were added in this system.

During pre-electrolysis, the product recovery traps were bypassed. The product recovery traps contained acetic acid and were used to convert the trifluoroacetyl fluoride produced in the ECF step to trifluoroacetic acid. The aqueous traps used potassium iodide to neutralize any oxidants, such as OF_2 and F_2. Any HF reaching the aqueous trap would pass into the solution. Therefore, only nitrogen, hydrogen and trace organics exited the system. For safety an auxillary blowout system was also attached to the reactor.

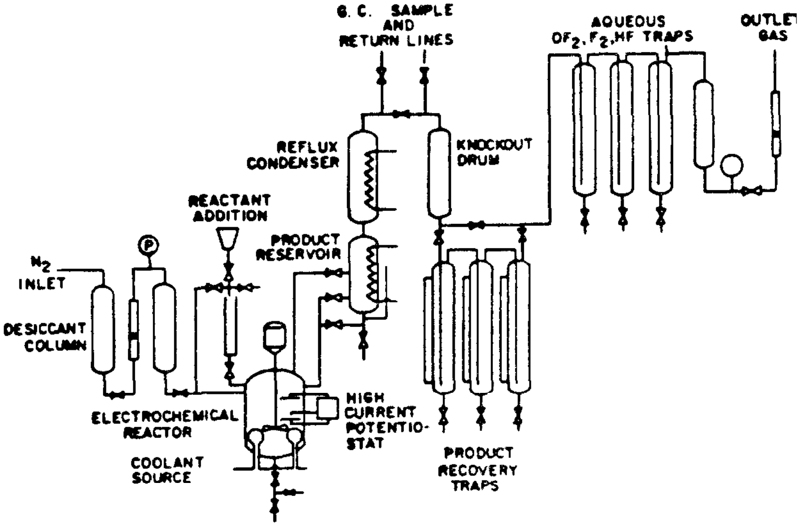

Fig. 2. Schematic of the Electrochemical Fluorination of Acetyl Fluoride System.

The reactor temperature could be maintained within 0.5°C of the setpoint temperature. The cooling source was a Neslab ULT-80 cooler, capable of providing up to 13 liters of methanol coolant per minute at temperatures down to -80°C.

The potential of the anodes in the reactor was controlled versus a Cu/CuF_2 reference electrode by a custom-built high current potentiostat which was powered by a high current power supply, Lambda Model LES-EE-02-OV, at 10 to 18 volts at 0 to 29 amperes.

The control and data acquisition system of this reactor has been described in detail previously and will not be repeated here. On-line sampling of the gases exiting the reactor was carried out during a run and analyzed by a gas-chromatograph.

In each experimental run, approximately 750 ml of AHF was added into the reactor. Pre-electrolysis of the AHF was then carried out at a constant cell voltage of 5.0 V in order to remove any water residue and to condition the anodes. When the cell current decreased to a constant value of 2 mA/cm^2, the first portion of the pre-electrolysis was considered complete. Typically, this required 10 to 20 amp-hours over an 8 to 10 hour period of time. The anodic potential during this period of time was monitored but not controlled.

Once the first portion of the pre-electrolysis was complete, the system was switched to constant anodic potential control at the potential to be used during the synthesis portion of the experiment. No reactant was added until the current decreased to a baseline value of 2 mA/cm^2. This second portion of the pre-electrolysis served to permit the anodic film to grow under the potential conditions to be employed in the ECF step. The charge passed and the time elapsed during this portion varied depending on the potential applied.

The following general experimental conditions were employed in this study:

Anodic Potential	4.25 - 6.00 volts versus Cu/CuF_2
Reaction Temperature	0 - 15°C
Reactor Agitation	450 RPM
Initial Reactant Concentration	1.0 - 1.3 M.

The agitation at 450 RPM corresponds to an agitation Reynolds number of 66,000 in our system. At this Reynolds number, the global flow regime was turbulent.

The product recovery employed the following reaction:

$$CF_3COF + CH_3COOH \longrightarrow CF_3COOH + CH_3COF$$

The equilibrium for this reaction lies very far to the right [5]. Hence, bubbling the reactor effluent containing trifluoroacetyl fluoride through glacial acetic acid in the product recovery traps resulted in the production of trifluoroacetic acid and the regeneration of the acetyl fluoride reactant in excess acetic acid. This solution could then be diluted and analyzed by gas chromatography. Details of the analytic techniques are given elsewhere [6].

RESULTS AND DISCUSSION

Preliminary experimental runs were first carried out with acetyl fluoride as the starting material to determine the efficiency of the product recovery traps. The results showed that the first two traps contained all the trifluoroacetic acid recovered and that the product yield was better than 40%. A series of four experimental runs was then carried out under various operating conditions. The experimental conditions and the results obtained are presented in Table 1. Chemical yields of 36 to 45% and current efficiencies of 32 to 50% were obtained. Though some others have reported the need of conductivity additives for the ECF of acetyl fluoride, we obtained reasonable current density without employing any additives.

One of the major features of the fluorination process investigated in this study was the function of the anodes. Both the anodic corrosion rate and the effect of varying the anodic surface area to volume ratio was investigated. Figures 3 and 4 show the time dependent current characteristics for surface area to volume ratios of 0.144 cm^2/cm^3 and 0.288 cm^2/cm^3 respectively. Although at first glance these curves seem entirely different, each supports a surface area controlled reaction. Both figures show the current increasing even though reactant was being consumed. This was probably due to the growth of the anodic film and the corresponding increase in surface area, indicating a surface area controlled reaction mechanism.

TABLE 1

SUMMARY OF EXPERIMENTAL RESULTS FOR THE ELECTROCHEMICAL FLUORINATION OF ACETYL FLUORIDE

Run	Anode Potential (V vs Cu/CuF_2)	Cell Voltage (V)	Cell Temperature (°C)	Initial Reactant Concentration (M)	Anode Surface Area to Volume Ratio (cm^2/cm^3)	Conversion Efficiency (%)	Current Efficiency (%)	Energy Efficiency (%)
1*	5.25	6.24	10	1.20	0.144	--	--	--
2*	4.45	5.50	5	0.61	0.144	--	--	--
3	6.00	8.03	5	1.13	0.288	45	32	11
4	5.25	6.14	10	1.19	0.144	42	50	23
5	5.75	7.44	10	1.15	0.288	42	41	16
6	5.75	6.24	10	1.24	0.288	36	41	17

* preliminary runs

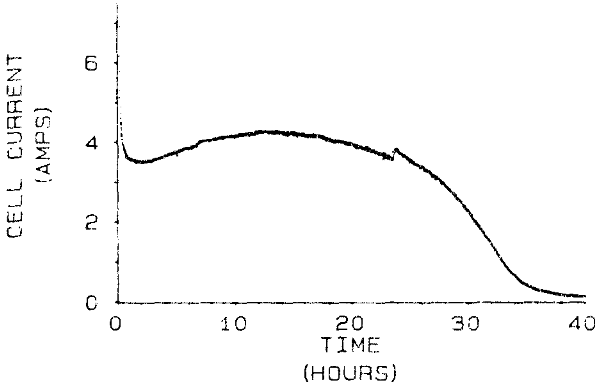

Fig. 3. Typical Current Profile for an ECF of Acetyl Fluoride Experiment Employing Two Electrode Packs.

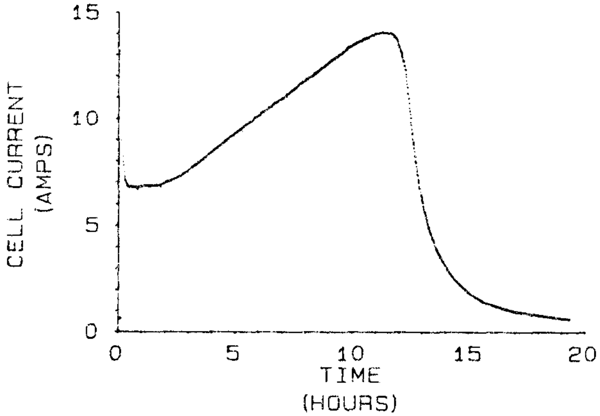

Fig. 4. Typical Current Profile for an ECF of Acetyl Fluoride Experiment Employing Four Electrode Packs.

In Figure 3, the current density reaches a maximum, remains there for the duration of the run, then drops off as reactant was consumed. In Figure 4, the current rises steeply and then decreases sharply. This is also consistent with a surface area controlled reaction mechanism, since with more available area, the growth of the anodic film proceeds at a faster rate. It is also plausible that there is a maximum for the growth of this film at a given potential that is reached in the case of the smaller electrode area but not in the case of the larger area. Figure 5 shows the current trace for a semi-batch run with the same surface area to volume ratio as Figure 4. Here the current seems to level off after the second reactant addition. This supports the postulate of a surface area controlled reaction.

The sharp tail off of the current at the end of the run is most probably due to a combination of factors including mass transfer limitation, increase in ohmic drop across the solution, and decrease in the conductivity of the anodic film.

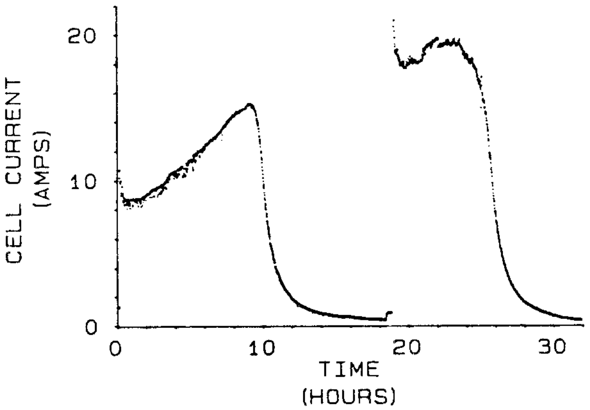

Fig. 5. Current Profile for a Semi-batch ECF of Acetyl Fluoride Experiment Employing Four Electrode Packs.

The rate of anodic corrosion was investigated by employing different electrode packs for the electrolysis and synthesis portions of the experiment. Table 2 contains the results of this study. The corrosion rate was one to three orders of magnitude greater for pre-electrolysis than for synthesis. This indicates that there is a fundamental difference in the anodic film with and without reactant present as corrosion is negligible with organics present. It was also observed that the electrolyte was often very dark during pre-electrolysis due to suspended corrosion products and then became clear upon the addition of reactant, suggesting that the organic may modify the corrosion product.

TABLE 2

RESULTS OF THE CORROSION OF NICKEL ELECTRODES

Run	Anode Potential (V vs Cu/CuF_2)	Average Anodic Weight Loss (g/cm^2)	Average Cathodic Weight Loss (g/cm^2)
1	5.25	0.0161	0.00125
2	4.45	0.00165	0.000435
3	6.00	0.0676	0.000306
4	5.25	0.0116	0.00337
5	5.75	0.00667	0.00210
6	5.75	0.00464	0.000750

Some workers observed an induction period for new nickel electrodes where charge was passed but no product was produced. Gas chromatographic analysis of the reactor effluent showed that for the production of trifluoroacetyl fluoride this is not the case. A peak corresponding to trifluoroacetyl fluoride appeared immediately upon reactant addition. However, the time dependent current traces show that the rate of production of trifluoroacetyl fluoride increases with the charge passed.

Watanabe [7] carried out potential decay measurements for ECF electrodes and determined that a great deal of fluorine was absorbed in the anodic film. Figure 6 shows the potential decay of the anodes observed in this study over a period of eight hours. This shows the film had a larger charge capacity which Watanabe suggested was due to the reduction of the absorbed fluorine. It should also be noted that the anodic overpotential is the major polarization for the ECF reaction carried out in this study. Assuming a thermodynamic potential of 2.85 V for ECF, the typical anode polarization was 3 volts compared to a cathode polarization of 0.5 volts.

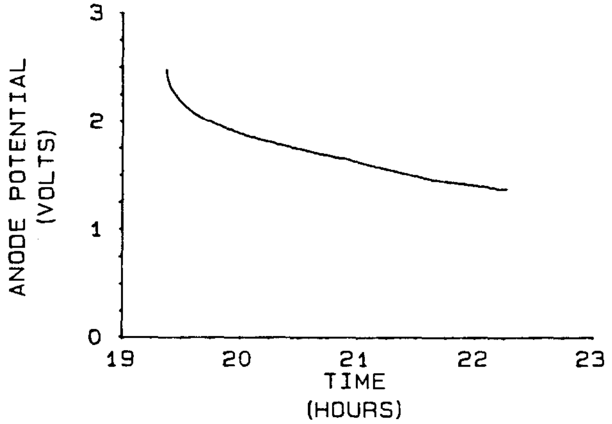

Fig. 6. Time-Dependent Potential Decay Profile of the Anode in an ECF Experiment

The conversion current and energy efficiencies for the experiments have been shown in Table 1. These efficiencies are based on product recovered and the actual efficiencies are probably higher. As can be seen from the data, the conversion efficiency is fairly consistent for the different experiments. The current efficiency, however, appears to be dependent on the anode potential with the lowest current efficiency found at the highest operating potential and vice-versa. Evidently a side reaction, such as fluorine evolution, increases at the higher potentials.

CONCLUSION

The electrochemical fluorination of acetyl fluoride to produce trifluoroacetyl fluoride in the modified Simons' reactor is successful. The product is recoverable as trifluoroacetic acid. Conversions obtained ranged from 36 to 45% based on product recovered.

The total cell current during the ECF of the acetyl fluoride was much lower than the mass transfer limiting current, indicating that the reaction was not under mass transfer control. The cell current was inversely related to the reactant concentration for the majority of the synthesis, indicating that the reaction was not under ohmic control. The data is consistent with a reaction controlled by the amount of surface area available on the anodic film. An increase in the cell current with time is then due to an increase in the surface area of the anodic film.

The corrosion rate of the nickel anodes is much lower in the presence of the organic reactant than the rate of corrosion in pure AHF. This indicates that the anodic reaction is modified by the presence of the organic.

The efficiency of converting acetyl fluoride to trifluoroacetyl fluoride ranged from 36 - 45% based on product recovered. The current efficiencies ranged from 31 - 50% also based on product recovered. The energy efficiencies ranged from 11 - 23%, with a trade off between reaction rate and energy efficiency.

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