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ANALYSIS OF THE PRODUCTS FROM THE ELECTROCHEMICAL FLUORINATION OF OCTANOYL CHLORIDE

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SUMMARY

The perfluorinated products from the electrochemical fluorination of octanoyl chloride were analyzed using several techniques. Capillary gas chromatography was used for quantitative analysis of the desired product, perfluorooctanoyl fluoride, and for perfluorinated cyclic ether by-products. Isopropyl ether was an effective solvent, and ethylbenzene served as an internal standard.

Acidimetric titration was used to quantify the amount of acid derivative products present in the sample. Since the products have limited solubility in water, alternative solvents were developed.

Taking advantage of the facile hydrolysis of the acyl fluoride product, the perfluorinated acid was isolated.

Details of the application of these chemical techniques to perfluorinated products and the corresponding results will be discussed.

INTRODUCTION

Electrochemical fluorination (ECF) is the replacement of hydrogen by fluorine, typically in an organic substrate, by an electrochemical process. The replacement is extensive throughout the molecule, except under unusual circumstances.

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This would seem to limit the possible range of perfluorinated products obtained. In the case of octanoyl chloride, however, a diversity of products was obtained. Besides the desired product, perfluorooctanoyl fluoride, ring closure products, perfluoroalkanes (POF), and smaller chain length acyl fluorides were also obtained.

All of these products are contained in a clear, dense, liquid perfluorinated product phase that is obtained from the ECF reactor. Organic chemistry specialists such as Nagase [1] and Rozhkov [2] have made detailed studies of the products from ECF. However, in an engineering investigation of ECF [3] it will be desirable to analyze the reaction products in real time using convenient and inexpensive analytical methods, if possible.

Thus, in this study, quantitative analysis of the products was achieved using capillary gas chromatography. Peak identification was performed using a combined gas chromatograph/mass spectrometer. Since the desired product is functionally an acid derivative, acidimetric titration was also attempted.

Details of the application of these analytical techniques to perfluorinated samples will be given in this paper.

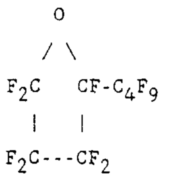
EXPERIMENTAL

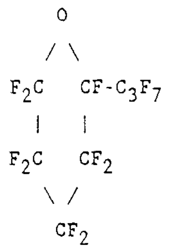
The gas chromatograph used in this investigation was a Hewlett Packard 5890A Gas Chromatograph. The detector was the standard thermal conductivity detector using a helium carrier gas. A fused silica capillary column 10 meters long with a 530 micron diameter gave good separation of product components. The column film was a standard Hewlett Packard type, crosslinked methyl silicone. The operating conditions of the instrument were as follows:

Carrier Gas-	helium (Matheson, 99.995 %)
Column Flow Rate-	12 ml/min
Column Head Pressure-	0.1 psig
Inlet Temperature-	200°C
Detector Temperature-	200°C

It should be noted that the column pressure is relatively low. This was necessary to aid the separation of two components that were evolved early in the separation. Injections were made with a silica needle through the dedicated capillary injection port.

There are several components to the product mixture that is obtained from the ECF of octanoyl chloride. The desired product is perfluorooctanoyl fluoride (POF) which is a straight-chain acyl fluoride, $C_7F_{15}COF$. This material is useful as a high performance surfactant. Perfluorinated cyclic ethers are formed by a ring closure reaction. They are a less desirable by-product, but they do have some value as an inert fluid. Both five- and six-membered rings are present:





In our electrochemical fluorination study, no attempt was made to investigate the ratio of these five and six-membered ring compounds under different experimental conditions because our main desired product is the straight-chain acyl fluoride.

The degradation of POF by a Kolbe process results in the formation of perfluoroheptane, C_7F_{16}. There is evidence that shorter-chain acyl fluorides are also present. This comes from the titration, which will be discussed later.

The greatest difficulty in the analysis was in finding an appropriate solvent for the perfluorinated liquid products. Water is an excellent selective solvent, which will be discussed later. Alcohols are useful, because the straight-chain perfluorooctanoyl fluoride (POF) converts to the ester form. This is an advantage in that POF is commercially available as the crystalline acid. Therefore, standard solutions can be prepared with the acid, which also esterifies. Successful gas chromatographic analysis has been performed using methanol [4] and ethanol [5]. The disadvantage to these solvents is that the perfluorinated cyclic ethers have poor solubility in alcohols. Due to the limited sensitivity of the thermal conductivity detector, solutions must not be too dilute. Therefore, a better solvent for the ethers was sought.

Ethyl ether could be an excellent solvent for all of the product components from the ECF of octanoyl chloride. However, its boiling point interferes with the lighter product components in the separation. Therefore isopropyl ether was chosen as the solvent for this analysis. It has the desired solvent properties, while its boiling point places the solvent peak separate from the other materials.

For quantitative analysis an internal standard was desired. Ethylbenzene has a boiling point favorable for the separation, and its peak shape is good for quantitative measurements.

The most difficult separation was between the two lightest components, perfluoroheptane and the cyclic ethers. Therefore, a simple temperature program was sufficient.

Typical temperature programming involves-

Initial Temperature- 30° C
Initial Time- 5 min
Rate- 30 degrees/min
Final Temperature- 150° C
Final Time- 5 min
Total Time- 14 min

The lightest components were best separated by a low initial temperature and a low column pressure.

Small sample sizes were used to maintain good peak shape. Best results were obtained with 1 microliter injections. A typical separation from a product sample is illustrated in Fig. 1. The order of evolution is perfluoroheptane (retention time (RT) =0.61 min), cyclic ethers (RT =0.77), isopropyl ether (RT =1.99), ethylbenzene (RT =7.58), and perfluorooctanoyl fluoride (RT = 9.13). The column was overloaded with the solvent, which

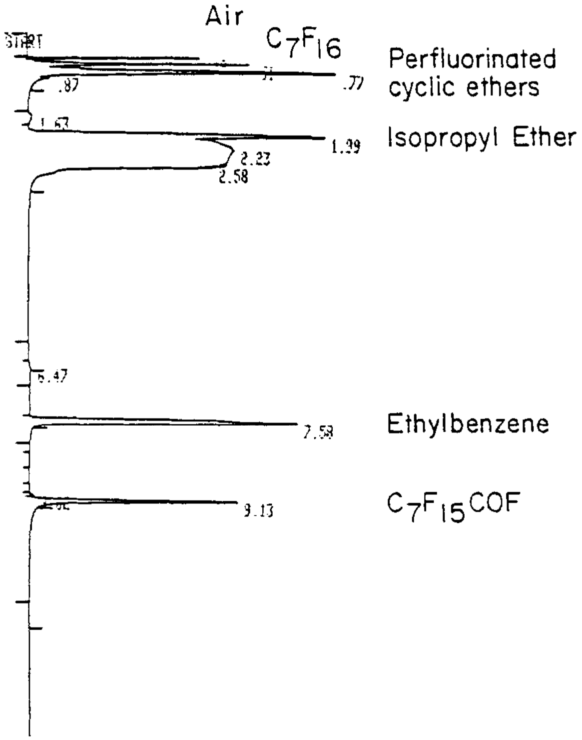


Fig. 1. Typical Gas Chromatographic Separation for the Products of Electrochemical Fluorination of Octanoyl Chloride.

caused the double solvent peak. The cyclic ether peak represents both the five- and six-membered rings.

Standard solutions were prepared to calibrate the compounds against the internal standard. A mixture of the cyclic ethers was provided by the 3M Company, and pentadecafluorooctanoic acid (Aldrich, 98 %) served as the standard for POF. The behavior of pentadecafluorooctanoic acid (POA) was precisely the same as that of POF in the gas chromatographic analysis with respect to both retention time and peak shape. No standard was available for perfluoroheptane, so the quantitative analysis of the product samples was somewhat limited.

Standard solutions were prepared with the following composition:

isopropyl ether-	90.1-97.3 weight %
ethylbenzene-	1.5 weight %
cyclic ether mixture-	1.2-8.4 weight %
pentadecafluorooctanoic acid-	1.7-7.4 weight %

Separate calibrations were performed for POF and the cyclic ethers.

RESULTS AND DISCUSSION

Gas Chromatographic Analysis

The ratio of the weight percent of a desired compound to the initial standard, ethylbenzene, is estimated by the ratio of the chromatographic areas of these compounds respectively. This relationship is then used for calibration. Fig. 2 shows the calibration characteristics of POA (serving as calibration for POF) and Fig. 3 shows the calibration characteristics of perfluorinated cyclic ethers. In Figure 2, excellent linear relationship is shown for the weight % ratio of POA to ethylbenzene up to 3.5%, with a least square regression coefficient of 0.996. In Figure 3, excellent linear relationship is also shown for the weight % ratio of perfluorinated cyclic ethers to ethylbenzene up to 5.0% with a least square regression coefficient of >0.999. In Figure 2, the intercept of the calibration line does not go through zero, because the peak shape of this calibration is less than ideal. The peak tails considerably, resulting in some loss in the integration process of the area.

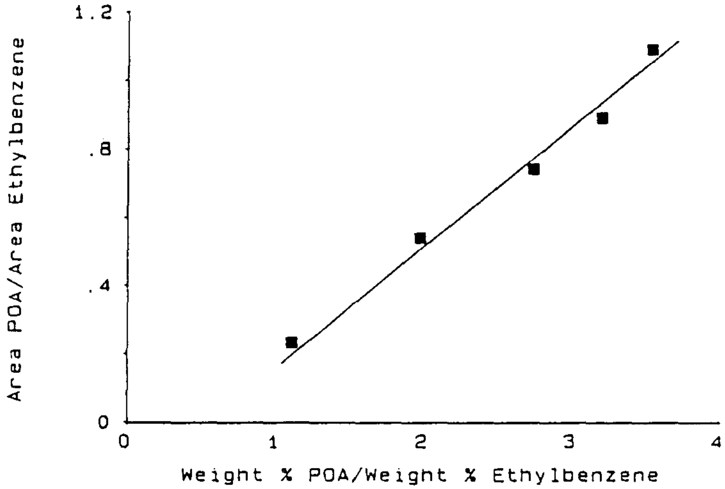


Fig. 2. Chromatographic Calibration of Pentadecafluorooctanoic (POA) Serving as the Calibration for Perfluorooctanoyl Fluoride (POF).

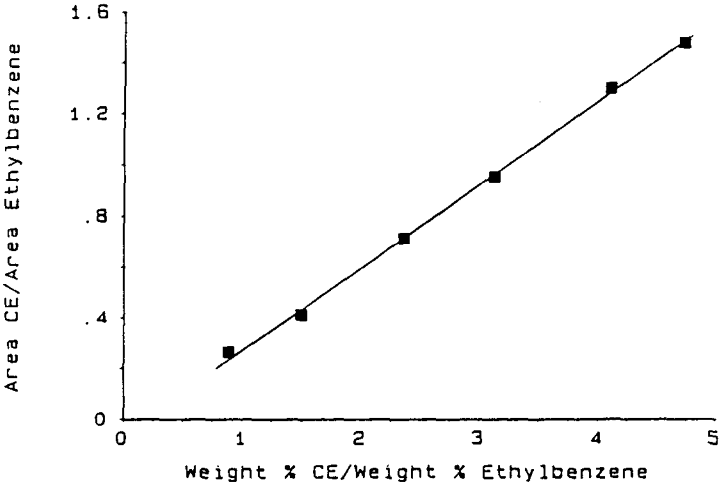


Fig. 3. Chromatographic Calibration of Perfluorinated Cyclic Ethers.

Based on the information derived from Figures 2 and 3, the product samples to be analyzed were prepared so that the quantity or the weight percent of the components in the sample were within the linear region of the calibration lines shown in Figures 2 and 3. Thus, the product sample was diluted prior to analysis. Typically, the dilution scheme involved:

isopropyl ether-	greater than 85 weight %
ethylbenzene-	about 1.3 weight %
product sample-	less than 10 weight %
pentadecafluorooctanoic acid-	1 to 2 weight %
total mass-	about 5 grams

Additional POA was added to the product sample to increase the area of the product peak for more reliable analysis. This became necessary for product samples during the latter part of an experimental run when the content of POF was relatively low.

The identity of the peaks was verified by analysis with a Hewlett Packard 5970C ChemStation, which combines a 5970B Mass Selective detector and a 5890A Gas Chromatograph. This instrument had a capillary column similar to that used for the Hewlett Packard 5890A gas chromatograph previously described except that the length was 25 meters and the diameter was 320 microns.

The mass spectrum for the straight-chain POF from a product sample is shown in Fig. 4. There is excellent agreement with the published spectrum for perfluorocaprylic acid [6]. The mass spectrum for the combined five- and six-membered cyclic ethers from the same product sample is shown in Fig. 5. Also, there is excellent agreement with the spectrum from the 3M standard solution. The mass spectrum for perfluoroheptane is shown in Fig. 6.

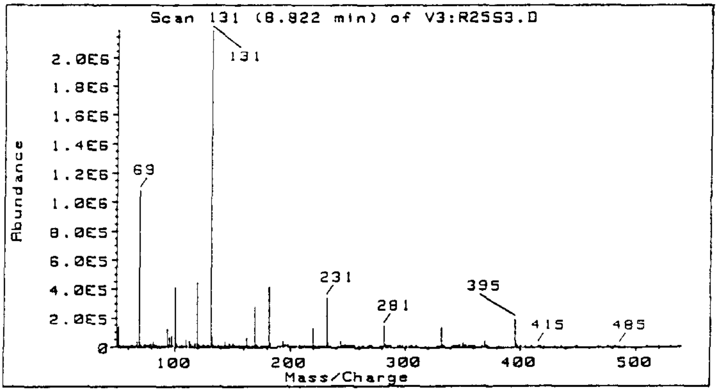


Fig. 4. Mass Spectrum for Perfluorooctanoyl Fluoride (POF).

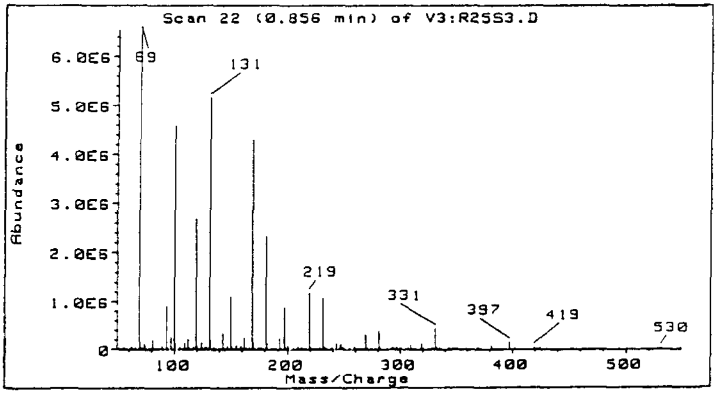


Fig. 5. Mass Spectrum for Perfluorinated Cyclic Ethers.

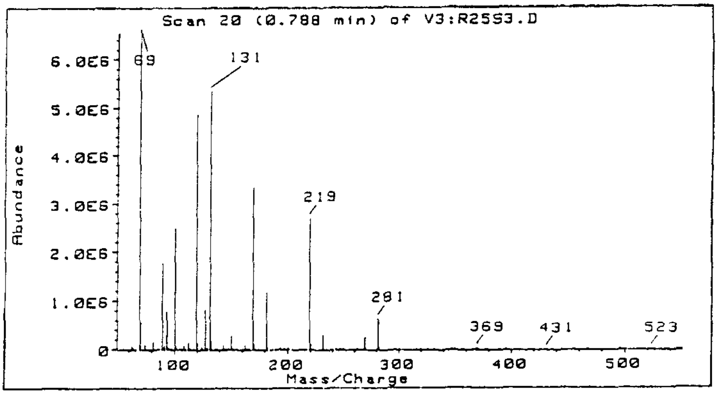


Fig. 6. Mass Spectrum for Perfluoroheptane

Titration Method and Results

As mentioned, a titration scheme was also included in this analysis. The aqueous titration of POF takes place in two steps:

$$\begin{array}{llllllll} 1. & C_7F_{15}COF & + & H_2O & = & C_7F_{15}COOH & + & HF \\ & HF & + & NaOH & = & NaF & + & H_2O \\ 2. & C_7F_{15}COOH & + & NaOH & = & C_7F_{15}COONa & + & H_2O \end{array}$$

$$\text{Total: } C_7F_{15}COF + 2NaOH = C_7F_{15}COONa + NaF + H_2O$$

The acyl fluoride is hydrolyzed to the acid, which creates HF to consume one equivalent of NaOH. The second equivalent is consumed in converting the acid to the sodium salt. Anhydrous hydrogen fluoride is the electrolyte used in the ECF process, so a small amount of HF may be dissolved in the products. This HF will be consumed in the first step. Therefore quantitative results were calculated using the NaOH added between the first and second end-point of the titration.

The solubility of the perfluorinated acid in water is 0.414 g in 100 ml at 22°C [7]. The solubility of the perfluorinated ethers is very low, so phase separation occurs if excessive water is used. If titration is attempted in water alone as a solvent, the reactions become very slow. All of the perfluorinated products are soluble in acetone. Rapid titration was achieved using product samples in mixtures with the following composition:

product sample- 0.5-1 gram
acetone- 40 ml
water- 4 ml

The sodium hydroxide titrant was diluted with ethanol. From a 1 molar aqueous sodium hydroxide solution, ethanol was added to dilute to 0.1 molar. With this mixture of solvents, titration is rapid, repeatable, and occurs in one phase.

The pH was monitored through the titation by using a standard pH electrode and pH meter, Orion Research Model 811. Two endpoints are observed; one near pH 4, and the other near pH 8.

The results of titration for two samples were compared with the results from gas chromatography.

Sample 1: weight % POF by titration: 25.4
by GC : 17.5
Sample 2: weight % POF by titration: 21.4
by GC : 17.3

The titration results indicate more acid present than is accounted for from the GC results.

Product Purification

It was mentioned that the solubility of the cyclic ethers is low in water. Thus water can be used as a selective solvent to isolate the straight-chain POF in its crystalline acid form. The hydrolysis of POF is facile, but the isolation of pentadecafluorooctanoic acid requires some special treatment due to solubility effects.

As previously mentioned, the solubility of POA in water is not very large. The solubility of the sodium salt is 21.35 grams per 100 ml at 22°C [7], which is considerably higher. The first step in the purification process is to separate the product mixture into two phases using aqueous sodium hydroxide solution. A dense cloudy layer containing the ethers settles to the bottom. The top aqueous layer is clearer, but also somewhat cloudy.

The aqueous layer is easily extracted with a separatory funnel. Then sulfuric acid is added to convert the sodium salt back to the acid form. After the sulfuric acid has been added a dense, yellow colored phase forms at the bottom of the system. The remaining liquid is somewhat cloudy. The colored phase is a gel containing the pentadecafluorooctanoic acid. In order to crystallize the acid from the mixture, it should be placed in a freezer of at least -10°C. When the crystallization is complete, the liquid becomes clear, and the acid is on the bottom as small white crystals. The crystals can then be filtered and/or centrifuged and dried. When drying, the temperature should be lower than the melting point of the acid, 55°C.

CONCLUSIONS

Real time perfluorinated product analysis for the electrochemical fluorination process is possible without costly and sophisticated analytical equipment. Capillary gas chromatography provides a rapid, simple, and readily available analytical technique. Choosing a suitable solvent is critical, and ethers work well for products from the ECF of octanoyl chloride. If standard compounds are available, quantitative analysis is convenient using an internal standard. In the octanoyl chloride system calibrations were obtained for two compounds over a relatively small composition range.

Using appropriate solvents, aqueous titration of perfluorinated acids is possible. However, titration cannot distinguish between acids of different carbon chain length.

Pentadecafluorooctanoic acid can be isolated and purified from an ECF product sample by separating the cyclic ethers out with aqueous sodium hydroxide. The resulting sodium salt can be converted to the acid form with sulfuric acid, and the acid crystallizes out under cooling.

These analytical techniques were specifically designed to support the engineering investigation of the ECF of octanoyl chloride. Quick and reliable determination of product compositions gives valuable information on the progress of the process. From the variety of products obtained, ECF clearly has an extremely complicated mechanism. Analytical techniques like those used in this investigation when applied to ECF investigations may determine the nature of this mechanism.

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REFERENCES

1 H. Baba, K. Kodaira, S. Nagase and T. Abe, Bulletin of the Chemical Society of Japan, 51 (1978) 1891.

2 I. N. Rozhkov, A. V. Bukhtiarov, E. G. Gal'pern, Il L. Knunyants, Doklady Akademii Nauk SSSR, 199 (1971) 598.

3 H. W. Prokop, H-J Zhou, S-Q Xu, C-H Wu, S. R. Chuey, and C. C. Liu, J. Fluorine Chem., 43 (1989) 257.

4 S. R. Chuey, M.S. Thesis, Case Western Reserve University, November (1988).

5 F. G. Drakesmith and D. A. Hughes, Journal of J. Fluorine Che 32 (1986) 103.

6 E. Stenhagen, S. Abrahamsson, eds., 'Atlas of Mass Spectral Data', Vol. 3, Interscience Publishers, 2174 (1969).

7 Personal Communication, Chung-Ho Wu, The China Petrochemical Development Company, Taiwan.