Preparation of Perfluorocarboxylic Acids from Esters by Electrochemical Fluorination[*]

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Perfluorocarboxylic acids have been prepared from carboxylic acids, acid halides, acid anhydrides and acid amides, ketones, ethers etc. by electrochemical fluorination[1-4].

In a previous paper[5], it was shown that perfluorocarboxylic acids were prepared in a significant yield from alcohols which were known to give only fluorocarbons by electrochemical fluorination[1,6]. A possible mechanism of the fluorination of alcohols to perfluorocarboxylic acid fluorides was assumed to involve the first attack by fluorine on α-carbon atom of the alcohols, and dehydrofluorination followed by exhaustive fluorination of acid fluorides formed as intermediates to perfluoroacid fluorides.

The present paper deals with the work extended further to the fluorination of esters to obtain perfluorocarboxylic acids.

So far, there has been no detailed report on the electrochemical fluorination of simple esters. Simons[2] carried out the fluorination of butyl acetate and made decafluorobutane.

In the present series of work, ethyl, propyl and butyl acetates, ethyl, propyl and butyl propionates, and ethyl, propyl and butyl butyrates were fluorinated and trifluoroacetic, perfluoropropionic, and perfluorobutyric acids were obtained in good yields.

Again, the mechanism of dehydrofluorination at α-carbon atom of alcohols which takes place after hydrofluorolysis of esters into carboxylic acid fluorides and alcohols, could be applied to the formation of perfluorocarboxylic acid fluorides from esters.

The perfluorocarboxylic acid fluorides formed were converted into perfluorocarboxylic acids by treatment with water. No detectable amount of partially fluorinated esters and alcohols were found in the residue in the electrolytic cell but the presence of acid fluorides and unreacted esters, etc. was confirmed.

Experimental

Materials.—*Esters.*—Special or first grade commercial reagents were used after distillation through a fractionation column. Some of the esters were prepared in the usual manner in this laboratory.

Hydrogen Fluoride.—Hydrogen fluoride purity of 99.4% was supplied from a commercial cylinder.

Apparatus.—The apparatus used for this work essentially consisted of an electrolytic cell, a sodium fluoride tube, and an absorber, as described previously[5].

The electrolytic cell of 1 l. in capacity was a 10-cm. cylindrical nickel vessel provided with a copper condenser at the top to cool down vaporizing hydrogen fluoride and a drain at the bottom, and having 8 and 9 pieces of nickel plates (0.5 mm. in thickness) as anodes and cathodes, fastened together, suspended alternately from the top, and insulated from each other by Teflon pieces. The distance between the plates was 1.7 mm. and the effective surface area of the anodes and cathodes was 9.2 dm^2. A copper tubing was provided inside the cell to keep the optimum temperature by circulation of ice water during the reaction.

The sodium fluoride tube was an iron pipe containing sodium fluoride pellets to remove hydrogen fluoride.

The absorber used was a pair of polyethylene bottles containing 200 and 50 ml. of water.

Procedure.—One liter of hydrogen fluoride was introduced into the cell through the polyethylene container, and electrolysis was carried out without a sample to remove a trace of water in the hydrogen fluoride at an average of 5.2 V. for about 13 amp. hr. in nitrogen atmosphere. About 35 g. of the sample was then dissolved in this solution and electrolysis was carried out with the anodic current density of 2.5 to 3.5 amp./dm^2 at an average of 4.8 V., at 4~6°C for designated amp. hr. At the end, the voltage rose up to 5.2~5.3 V.

It was found that the amount of the electricity used up to this point corresponded to about 1.3 times that assumed to be required to form fluorine with discharging fluoride ion which would substitute with hydrogen in the sample and combine with it to form hydrogen fluoride.

The gaseous product generated from the cell, containing fluorocarbons, oxygen difluoride, perfluoro-acid fluorides, hydrogen, etc. was passed through

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[1] J. H. Simons et al., *J. Electrochemical Soc.*, **95**, 47 (1949).

[2] J. H. Simons, U. S. Pat., 2519983 (1950).

[3] A. R. Diesslin, E. A. Kauck and J. H. Simons, U. S. Pat., 2567011 (1951); U. S. Pat, 2593737 (1952).

[4] E. A. Kauck and A. R. Diesslin, *Ind. Eng. Chem.*, **43**, 2332 (1951).

[5] S. Nagase and R. Kojima, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), in press.

[6] J. Burdon and J. C. Tatlow, "Advances in Fluorine Chemistry", Vol. 1, Ed. by M. Stacey, J. C. Tatlow and A. G. Sharpe, Butterworths Scientific Publications Ltd., London (1959), p. 157.

the condenser and the sodium fluoride tube, and bubbled through water in the absorber where the perfluoro-acid fluorides reacted, and converted into perfluorocarboxylic acids. In this system, the gases which are inert to water should escape as gases.

When the reaction was over, the hydrogen fluoride in the cell was distilled into the polyethylene container which was used repeatedly by adding it into the new hydrogen fluoride for the next run, but for different kinds of esters, hydrogen fluoride freshly supplied from the cylinder was used. About 50 ml. of a residue consisting mainly of hydrogen fluoride remained at the bottom of the cell and its other components were investigated further by the method described earlier⁵⁾.

The aqueous solution of the perfluorocarboxylic acids in the absorber was neutralized with sodium carbonate, filtered and the filtrate was dried. The sodium perfluorocarboxylates formed were then extracted with absolute ethanol.

Quantitative analysis of the products was made by the base line method with potassium bromide pellet infrared absorption spectrum using 11.88 μ (for sodium trifluoroacetate), 9.68 μ (for sodium perfluoropropionate), and 10.65 μ (for sodium perfluorobutyrate) as key bands. The standard sodium carboxylates were prepared from trifluoroacetic acid secured from the Eastman Kodak Co., and perfluoropropionic and perfluorobutyric acids secured from the Minnesota Mining and Manufacturing Co. by treatment with sodium carbonate.

When several runs were repeated, the electrodes were stained with a grey substance, which was removed by electropolishing in 0.5% of potassium carbonate solution.

Results and Discussion

The effect of anodic current density on the yield was mainly examined in a similar manner as in the fluorination of alcohols. Trifluoroacetic acid was obtained from ethyl acetate and the results are shown in Table I. The yields shown were calculated on the basis that 1 mol. of ethyl acetate would give 2 mol. of sodium trifluoroacetate. The fluorination of ethanol also yielded trifluoroacetic acid, but the yield was usually less than that in the case of ester.

The calculation of current efficiencies shown was based on the amount of the electricity assumed to be required to form fluorine with a discharging fluoride ion which would substitute hydrogen in the ester and combine with it to form hydrogen fluoride. This means that the electricity to make 8 mol. of fluorine would be required for the fluorination of 1 mol. of ethyl acetate to form 2 mol. of sodium trifluoroacetate.

The results obtained from the fluorination of propyl acetate, from which trifluoroacetic and perfluoropropionic acids were obtained, are shown in Table II. The yields shown were also calculated on the basis that 1 mol. of propyl acetate would give 1 mol. of sodium trifluoroacetate and 1 mol. of sodium perfluoropropionate, which means that the acyl and the alkyl groups in the ester would give perfluorocarboxylic acids whose number of carbon atoms corresponds to those of the acyl and the alkyl group in the ester.

TABLE I. FLUORINATION OF ETHYL ACETATE

Electricity passed: 211 amp. hr.

Sample taken: 34.5 g.

D_A[a)] amp./dm²	Product obtained g.	Yield %	Current efficiency %
2.5	45.6	43.4	34.0
2.7	47.2	44.9	35.2
3.0	52.0	49.5	38.8
3.3	54.2	51.6	40.5
3.5	54.9	52.3	41.0

a) D_A: Anodic current density.

The current efficiency was also calculated by the same method as for ethyl acetate, i. e. the electricity assumed to make 10 mol. of fluorine would be required for the fluorination of 1 mol. of propyl acetate to form 1 mol. of sodium trifluoroacetate and 1 mol. of sodium perfluoropropionate.

The results obtained from the fluorination of butyl acetate, ethyl, propyl and butyl propionates, and ethyl, propyl and butyl butyrates are shown in the Tables. All of the yields and current efficiencies shown were calculated in the same way as was mentioned above.

It was found that the yield of the perfluorocarboxylic acid obtained from the fluorination of propyl propionate or butyl butyrate was much higher than that from propyl or butyl alcohol, but the degree of cleavage which would result in the formation of perfluorocarboxylic acids consisting of a smaller number of carbon atom than that of corresponding alcohol, or acyl or alkyl group in the ester was essentially the same in alcohols and esters.

It is of interest to know which side of the ester, acyl or alkyl group, would give perfluorocarboxylic acid more easily. Comparison between the results obtained from butyl acetate and ethyl butyrate or butyl propionate and propyl butyrate indicated that perfluorobutyric acid was obtained in better yield from ethyl and propyl butyrates than from butyl acetate and butyl propionate. This showed that perfluorocarboxylic acids are formed more easily from acyl than alkyl group in the ester.

When the number of carbon atoms increased in the ester, the degree of cleavage increased, as is usually observed in electrochemical fluorination. For example, propyl acetate gave sodium trifluoroacetate and sodium perfluoropropionate in molar ratio of about 1 to 0.9, but butyl acetate gave sodium trifluoroacetate

TABLE II. FLUORINATION OF PROPYL ACETATE
Electricity passed: 228 amp. hr.

Sample taken g.	D_A amp./dm^2	Product obtained g.	Yield %	Current efficiency %	Composition[a)]	
					CF_3COONa	C_2F_5COONa
34.5	2.5	35.7	32.7	26.1	46	54
34.5	2.7	42.0	38.5	30.7	45	55
34.5	3.0	34.3	31.5	25.1	45	55
34.6	3.3	36.7	33.6	26.8	44	56
34.5	3.5	46.3	42.5	33.8	46	54

a) The composition of the products analyzed by infrared spectrophotometer is given in weight per cent.

TABLE III. FLUORINATION OF BUTYL ACETATE
Electricity passed: 240 amp. hr.

Sample taken g.	D_A amp./dm^2	Product obtained g.	Yield %	Current efficiency %	Composition, wt. %		
					CF_3COONa	C_2F_5COONa	C_3F_7COONa
34.6	2.5	32.7	29.5	23.5	60	2.4	38
34.5	2.7	27.1	24.5	19.4	63	1.9	33
34.5	3.0	32.7	29.6	23.5	56	4.7	40
34.5	3.3	30.8	27.9	22.2	64	1.9	34
34.6	3.5	39.7	35.8	28.6	54	2.7	43

TABLE IV. FLUORINATION OF ETHYL PROPIONATE
Electricity passed: 228 amp. hr.
Sample taken: 34.5 g.

D_A amp./dm^2	Product obtained g.	Yield %	Current efficiency %	Composition, wt. %	
				CF_3COONa	C_2F_5COONa
2.5	17.2	15.8	12.6	46	54
2.7	38.9	35.7	28.4	45	55
3.0	43.4	39.8	31.7	44	56
3.3	35.1	32.2	25.7	46	54
3.5	53.5	49.1	39.1	47	53

TABLE V. FLUORINATION OF PROPYL PROPIONATE
Electricity passed: 240 amp. hr.
Sample taken: 34.5 g.

D_A amp./dm^2	Product obtained g.	Yield %	Current efficiency %	Composition, wt. %	
				CF_3COONa	C_2F_5COONa
2.5	29.6	26.7	21.3	7.3	93
2.7	33.2	29.9	23.9	5.1	95
3.0	36.2	32.6	26.1	6.8	93
3.3	38.5	34.7	27.7	5.3	95
3.5	38.6	34.8	27.7	7.1	93

TABLE VI. FLUORINATION OF BUTYL PROPIONATE
Electricity passed: 250 amp. hr.
Sample taken: 34.5 g.

D_A amp./dm^2	Product obtained g.	Yield %	Current efficiency %	Composition, wt. %		
				CF_3COONa	C_2F_5COONa	C_3F_7COONa
2.5	30.3	27.1	21.5	6.5	65	28
2.7	30.7	27.5	21.7	6.9	67	26
3.0	33.6	30.0	23.8	7.7	62	31
3.3	29.7	26.6	21.1	7.8	64	29
3.5	43.1	38.6	30.6	6.3	64	30

TABLE VII. FLUORINATION OF ETHYL BUTYRATE

Electricity passed: 240 amp. hr.
Sample taken: 34.5 g.

D_A	Product obtained	Yield	Current efficiency	Composition, wt, %		
amp./dm^2	g.	%	%	CF_3COONa	C_2F_5COONa	C_3F_7COONa
2.5	31.8	28.9	23.1	50	3.9	46
2.7	27.3	24.8	18.8	49	4.9	46
3.0	35.6	32.3	25.9	56	2.3	42
3.3	35.8	32.5	26.0	55	2.8	43
3.5	32.4	29.4	23.5	49	4.1	47

TABLE VIII. FLUORINATION OF PROPYL BUTYRATE

Electricity passed: 250 amp. hr.
Sample taken: 34.5 g.

D_A	Product obtained	Yield	Current efficiency	Composition, wt. %		
amp./dm^2	g.	%	%	CF_3COONa	C_2F_5COONa	C_3F_7COONa
2.5	24.2	21.7	17.2	6.3	60	34
2.7	31.3	28.0	22.2	6.2	59	35
3.0	31.5	28.2	22.3	6.4	55	38
3.3	28.0	25.1	19.9	6.2	56	38
3.5	30.1	26.9	21.3	6.3	58	36

TABLE IX. FLUORINATION OF BUTYL BUTYRATE

Electricity passed: 258 amp. hr.
Sample taken: 34.5 g.

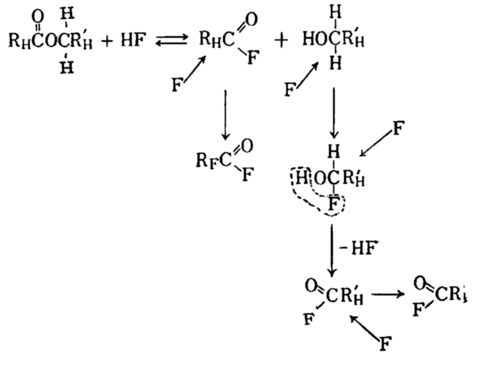
D_A	Product obtained	Yield	Current efficiency	Composition, wt. %		
amp./dm^2	g.	%	%	CF_3COONa	C_2F_5COONa	C_3F_7COONa
2.5	19.0	16.8	13.4	9.1	13	78
2.7	22.2	19.7	15.6	8.8	8.8	82
3.0	26.0	23.0	18.3	9.4	7.1	83
3.3	31.1	27.5	21.9	8.8	6.6	85
3.5	36.8	32.5	25.9	7.1	5.4	87

and sodium perfluorobutyrate in molar ratio of about 1 to 0.4, which indicates that butyl radical is degradated considerably as compared with propyl radical.

In the fluorination of alcohols, the maximum yield of perfluorocarboxylic acids was obtained with anodic current density of 3.3 amp./dm^2, and the yield decreased sharply with higher or lower current densities, irrespective of the kind of alcohols used, but there seemed to be no such simple relationship between the anodic current density and yield for the esters within the range of the current density applied. However, the yield generally increased with increasing current density.

The presence of a small amount of unreacted ester remaining in the residue in the cell along with the acetyl fluoride and partially fluorinated carboxylic acid fluorides was confirmed. The grey precipitate consisting mainly of nickel and copper fluorides was also found in the residue.

The mechanism of the fluorination of esters to form perfluorocarboxylic acid fluorides, although this reaction obviously could and probably did follow different routes simultaneously, might involve, in the first place, hydrofluorolysis of the esters in hydrogen fluoride to form acid fluorides and alcohols as shown below. Alcohols formed in this way would be converted into acid fluorides through the mechanism of dehydrofluorination at the α-carbon atom.



In these formulae, R_H and R_H' are hydrocarbon radicals, and R_F and R_F' are perfluorocarbon radicals. Acid fluorides R_H–COF and R_H'–COF thus formed would be fluorinated further to perfluorocarboxylic acid fluorides.

Conclusion

1) Perfluorocarboxylic acids were obtained from esters in a good yield by electrochemical fluorination and the relationship between anodic current density and yield was examined. Generally, the yield increased with increasing anodic current density.

2) The result of electrochemical fluorination of esters was compared with that of alcohols. A better yield was obtained from the esters.

3) The presence of a larger number of carbon atoms in the acyl or alkyl group in the ester caused more degradation than those of smaller numbers.

4) The mechanism of the formation of perfluorocarboxylic acid fluorides from esters was discussed.

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