Electrochemical Fluorination of 2, 2, 3, 3-Tetrafluoro-1-propanol

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Earlier work[1] of the present authors has shown that the electrochemical fluorination of alcohols gives perfluorocarboxylic acids in a significant yield. The present paper describes work extended further to the fluorination of C3 fluoroalcohol, 2, 2, 3, 3-tetrafluoro-1-propanol. The fluorocarboxylic acid with the corresponding number of carbon atoms, 3*H*-tetrafluoropropionic acid, which is easily obtained by oxidation from the C3 fluoroalcohol, was also fluorinated for the sake of comparison.

It is well known that the effect of enhancing the oil repellency of cotton fabrics treated by derivatives of perfluorocarboxylic acids or fluoroalcohols is markedly lessened if one hydrogen atom is present, instead of fluorine, at the ω-position of these fluorochemicals[2]. The ω-hydrogen of fluoroalcohols is relatively stable to chlorination[3]. From these facts, along with the results obtained from a series of electrochemical fluorinations of esters[4], ketones[5], aldehydes[6] and ethers[7], undertaken in order to prepare perfluorocarboxylic acids, the electrochemical fluorination of fluoroalcohols seemed of interest 2, 2, 3, 3-tetrafluoro-1-propanol was taken up.

No report has been made on the fluorination of fluoroalcohols. As expected, the ω-hydrogen was substituted for by fluorine, and perfluoropropionic acid containing a small amount of trifluoroacetic acid was obtained in quite a good yield from 2, 2, 3, 3-tetrafluoro-1-propanol. The yield was much higher than that obtained from propanol[1]. On the other hand, the amount of perfluorocarboxylic acid obtained from 3*H*-tetrafluoropropionic acid was extremely small.

The mechanism of the formation of perfluorocarboxylic acid fluorides from the fluoroalcohols should be similar to that for common alcohols[1].

Experimental

Materials.—2, 2, 3, 3-Tetrafluoro-1-propanol, given for research purposes by the Osaka Metal Industries Co., was purified by fractional distillation. 3*H*-Tetrafluoropropionic acid was prepared in this laboratory from 2, 2, 3, 3-tetrafluoro-1-propanol by oxidation with potassium permanganate according to Berry's method[8]. Hydrogen fluoride of about 99.4% purity was furnished by the Osaka Metal Industries Co.

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Apparatus.—The apparatus used for this work consisted essentially of a nickel electrolytic cell of a 1 l. capacity, provided with a reflux codenser at the top and a drain at the bottom, a sodium fluoride pellet tube, and a pair of polyethylene bottles in which perfluorocarboxylic acid fluorides generated from the cell reacted with water and were converted into perfluorocarboxylic acids. In this system, gaseous products which are inert to water are allowed to escape as gases. Nickel electrodes with an effective surface area of 9.2 dm^2 were used as usual. The details of the apparatus have been fully described previously[1,4].

Standard Procedure.—Hydrogen fluoride (1 l.) was introduced into the cell, and, in order to remove a trace of water, electrolysis was carried out in a nitrogen atmosphere, prior to the addition of the sample, with the anodic current density of 2.7 A./dm^2 and at 5~6°C, until the cell voltage rose to 5.7 V. Then 35 g. (0.265 mol.) of 2, 2, 3, 3-tetrafluoro-1-propanol was introduced into the cell, and electrolysis was carried out with the anodic current density of 2.7 A./dm^2 at about 5.2~5.6 V. and at 5~6°C until the cell voltage rose to 6.0 V. The amount of electricity required for this fluorination reaction was 55.4 A. hr.; the same amout of electricity was supplied for the reaction under other current densities and temperatures.

In the case of 3*H*-tetrafluoropropionic acid, 38.7 g. (0.265 mol.) of the sample was used. The amount of electricity required to raise the cell voltage to 6.0 V. was 44.4 A. hr. at 5~6°C, with the anodic current density of 2.7 A./dm^2.

By the same method as has been reported before, perfluorocarboxylic acids were obtained as their sodium salts; these were analyzed quantitatively by the base-line technique of the infrared absorption spectrum.

Results and Discussion

Electrolysis was carried out under a variety of operating conditions, achieved by changing the current density and the cell temperature, in order to find the conditions which would make the fluorination reaction mild and which would give the products in a good yield. The results are shown in Table I. The calculation of the current efficiencies shown was based on the amount of electricity assumed to be required to form fluorine by discharging the fluoride ion which would substitute for hydrogen in the sample. This means that the amount of electricity corresponding to that needed for the formation of 3 mol. of fluorine would be required to convert 1 mol. of 2, 2, 3, 3-tetrafluoro-1-propanol into 1 mol. of sodium perfluoropropionate.

In general, the yield of perfluoropropionic acid increased with an increase in the anodic current density and in the temperature of fluorination, but the amount of degraded acid, trifluoroacetic acid, formed also increased. Under the reaction conditions used, perfluorocarboxylic acids were obtained in the highest yield with an anodic current density of 1.6 A./dm^2 and at 16°C. Though the ratio of trifluoroacetic acid to perfluoropropionic acid decreased when the reaction was carried out at a lower temperature (which shows the reaction to be milder), the yield of perfluorocarboxylic acids decreased considerably. The least degraded products were obtained by the reaction at −10°C, with an anodic current density of 2.7 or 1.6 A./dm^2. The product obtained at −10°C with an anodic current density of 1.1 A./dm^2 contained rather a higher percentage of trifluoroacetic acid. This might be attributed to the smaller degree of agitation brought about by the evolved gases and to the fact that the reaction was less mild, because the rate of gas evolution should be smaller under this condition.

It is interesting to note that the composition of the perfluorocarboxylic acids obtained

TABLE I. FLUORINATION OF 2, 2, 3, 3-TETRAFLUORO-1-PROPANOL

D_A* A./dm^2	Temp. °C	Product obtained g.	Composition wt. %		Yield mol. %			Current efficiency %
			CF_3COONa	C_2F_5COONa	CF_3COONa	C_2F_5COONa	Total	
2.7	16	22.1**	11	89	6.8	39.9	46.7	34.5
2.7	5~6	22.5	8.0	92	4.9	42.1	47.0	35.2
2.7	−10	13.7	5.8	94	2.2	26.2	28.4	21.5
1.6	16	29.0	11	89	8.9	52.3	61.2	45.5
1.6	5~6	18.2	8.1	92	4.1	33.9	38.0	28.7
1.6	−10	11.0	5.7	94	1.7	21.1	22.8	17.2
1.1	16	26.9	14	86	10.2	47.0	57.2	42.2
1.1	5~6	14.7	8.2	92	3.4	27.3	30.7	23.0
1.1	−10	9.4	7.9	92	2.0	17.5	19.5	14.7

* Anodic current density

** The amount of electricity supplied for this reaction is 41 A. hr., because the cell voltage rose to 6.2 V. at this point.

by the fluorination of 2, 2, 3, 3-tetrafluoro-1-propanol is almost identical with those obtained from propanol[1)], propyl propionate[4)], diethyl ketone[5)], or dipropyl ether[7)]. As expected, the composition of the products formed was not affected by the change in the anodic current density.

The mechanism for the formation of perfluorocarboxylic acid fluorides from fluoroalcohols is possibly similar to that for common alcohols[1)]. This involves the first attack by fluorine on the α-carbon atom of the fluoroalcohols, and dehydrofluorination followed by exhaustive fluorination of the fluorocarboxylic acid fluorides thus formed into perfluorocarboxylic acid fluorides.

For the sake of comparison, electrochemical fluorination of 3*H*-tetrafluoropropionic acid was carried out with an anodic current density of 2.7 A./dm^2 at 5∼6°C, and of 1.6 A./dm^2 at 16°C and at 5∼6°C. By these reactions, the sample was degraded and fragmented seriously; only a trace of perfluorocarboxylic acids (0.2, 0.2 and 0.1 g. respectively) was obtained as their sodium salts. The product consisted of trifluoroacetic acid and perfluoropropionic acid in the ratio of 68:32, 61:39, and 60:40 under the respective reaction conditions given above. One reason for this result might be that given by Simons et al.[9)] for the electrochemical fluorination of carboxylic acids. 3*H*-Tetrafluorocarboxylic acid is a highly fluorinated acid, strong enough to form the $HC_2F_4CO_2^-$ ion in hydrogen fluoride; the Kolbe-type electrochemical process would then decompose this ion into fluorocarbons and carbon dioxide.

With both samples, a trace of polymeric material (0.2∼0.3 g.) was found in the residue in the electrolytic cell.

Summary

Perfluoropropionic acid, accompanied by a small amount of trifluoroacetic acid, was obtained in a good yield by the electrochemical fluorination of 2, 2, 3, 3-tetrafluoro-1-propanol. The yield or current efficiency increased with an increase in the anodic current density and cell temperature. Although the yield decreased at lower temperatures, the reaction became milder, giving a smaller amout of trifluoroacetic acid in the product. The composition of the perfluorocarboxylic acids obtained by this fluorination reaction is very similar to that of those obtained by the fluorination of propanol, propyl propionate, diethyl ketone, and dipropyl ether. Only a trace of perfluorocarboxylic acid was formed by the electrochemical fluorination of 3*H*-tetrafluoropropionic acid.

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