*Electrochemical Fluorination of Aldehydes**

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It has been shown in previous papers[1,2] that perfluorocarboxylic acids are prepared by electrochemical fluorination from alcohols and esters in a significant yield. A possible mechanism for the formation of perfluorocarboxylic acid fluorides from alcohols was suggested to involve the first attack by fluorine on the α-carbon atom of the alcohols, and dehydrofluorination followed by exhaustive fluorination of the acid fluorides formed into perfluorocarboxylic acid fluorides. In this process, it is possible to consider the formation of aldehydes as an intermediate, though not actually isolated, at the next step of the dehydrofluorination, before the formation of the acid fluorides.

With esters, the mechanism was assumed to start with the hydrofluorolysis of the esters in hydrogen fluoride to form acid fluorides and alcohols. The latter would then be converted into acid fluorides by the mechanism involving dehydrofluorination at the α-carbon atom. Perfluorocarboxylic acid fluorides would be formed by exhaustive fluorination of these two kinds of acid fluorides.

On the basis of these previous works and from the results of the fluorination of ketone[3], which gave perfluorocarboxylic acids in a reasonable yield, the electrochemical fluorination of aldehydes was attempted with the expectation that perfluorocarboxylic acids could be prepared from aldehydes.

So far, very little attention has been paid to the fluorination of aldehydes. Simons[4] carried out the electrochemical fluorination of butyraldehyde and obtained perfluoropropane. In the present work, acetaldehyde, propionaldehyde, butyraldehyde and aldol, as well as paraldehyde, were fluorinated under various anodic current densities (2.5~3.5 amp./dm^2). This treatment afforded trifluoroacetic acid, a mixture of trifluoroacetic acid and perfluoropropionic acid, or a mixture of trifluoroacetic acid, perfluoropropionic acid, and perfluorobutyric acid. Generally, however, the yield and current efficiency were relatively lower than those obtained in alcohols[1], esters[2], ketones[3] and some unsaturated compounds[5], because of considerable fragmentation or polymerization. No formation of a detectable amount of partially fluorinated aldehydes or perfluoroaldehydes could be confirmed throughout the reaction. Acid fluorides, unreacted aldehydes, and a tarry polymeric substance were found in the residue in the electrolytic cell.

The possible major route of the formation of perfluorocarboxylic acid fluorides from aldehydes may involve the fluorination-fragmentation of the ringed para-type polymer of the aldehyde which is in equilibrium with the aldehyde in hydrogen fluoride.

Experimental

Materials. — *Aldehydes.* — Special or first grade commercial reagents were used after distillation, but aldol (first grade) in a glass ampoule (25 g.) was used without further purification. Acetaldehyde was prepared in the usual manner from paraldehyde.

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

Apparatus.—The apparatus used for this work essentially consisted of an electrolytic cell provided with a reflux condenser at the top and a drain at the bottom, a sodium fluoride tube, and a pair of polyethylene bottle absorbers. The details have been described in previous papers[1,2].

Standard Procedure.—One liter of hydrogen fluoride was placed in the cell and, prior to the addition of the sample, in order to remove a trace of water in hydrogen fluoride, electrolysis was carried out in a nitrogen atmosphere, with an anodic current density of 2.7 amp./dm^2 until the cell voltage rose to 5.5 V. Twenty-five grams of the sample were then introduced into the cell, and electrolysis was carried out with an anodic current density of 3.3 amp./dm^2 at about 4.8~5.2 V. until the cell voltage again rose to 5.5 V.

The same amount of electricity as used under this current density was supplied for electrolysis under different current densities. The reaction temperature was kept at 4~6°C by the circulation of ice water through the copper tubing in the cell.

The gaseous product generated from the cell, containing perfluorocarboxylic acid fluorides, was passed through the reflux condenser and the sodium

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[1] S. Nagase and R. Kojima, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 1397 (1961).

[2] S. Nagase and R. Kojima, This Bulletin, **34**, 1468 (1961).

[3] S. Nagase, H. Baba and R. Kojima, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 2126 (1961).

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

[5] S. Nagase, H. Baba and R. Kojima, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 38 (1962).

fluoride tube and bubbled through water in then polyethylene absorber. The perfluorocarboxylic acid formed in the absorber was neutralised with sodium carbonate and filtered; the filtrate was the evaporated to dryness. The sodium perfluorocarboxylate thus formed was then extracted with absolute ethanol and dried. Quantitative analysis of the product thus prepared was made by means of the base line method of infrared absorption spectrum, as was previously described in detail[1].

A pair of glass traps, cooled by ice and by dry ice-acetone respectively, was connected with the absorber to collect the low-boiling fluorocarbons for the reaction under this current density.

Results and Discussion

Trifluoroacetic acid was obtained in a reasonable yield from acetaldehyde. The product from propionaldehyde was a mixture of trifluoroacetic acid and perfluoropropionic acid, while that from butyraldehyde and aldol consisted of trifluoroacetic acid, perfluoropropionic acid, and perfluorobutyric acid. However, the yield of these products was relatively low compared with those from alcohols[1], esters[2], ketones[3], or esters of unsaturated carboxylic acids[5], because of the great fragmentation or polymerization in the fluorination reaction. A considerable part of the perfluorocarboxylic acids obtained consisted of degraded acid, the number of whose carbon atoms was less than that of the starting aldehydes.

TABLE I. FLUORINATION OF ACETALDEHYDE

Electricity passed: 181 amp. hr.

D_A[a)] amp./dm^2	Product obtained g.	Yield mol. %	Current efficiency %
2.5	12.8	16.6	11.2
2.7	13.1	17.0	11.5
3.0	14.0	18.1	12.3
3.3	16.9	22.0	14.8
3.5	12.9	16.7	11.3

a) D_A: Anodic current density

The results of the fluorination of acetaldehyde, propionaldehyde, butyraldehyde, and aldol are given in Tables I, II, III and IV. 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 aldehyde and combine with it to form hydrogen fluoride.

This means that electricity enough to make 4, 6, 8 and 9 mol. of fluorine would be required for the fluorination of 1 mol. of acetaldehyde, propionaldehyde, butyraldehyde, and aldol respectively to yield perfluorocarboxylic acid fluorides the number of whose carbon atoms corresponds to those of the starting aldehydes.

In the case of the fluorination of alcohols[1] and in the majority of ketones[3], the highest yield of perfluorocarboxylic acids was found at the anodic current density of 3.3 amp./dm^2, irrespective of the kind of the sample used; with aldehydes, however, the yield appeared not to be much affected within the range of anodic current densities applied, although the highest yield was also found at 3.3 amp./dm^2 for most of the aldehydes.

It is interesting to note that the composition of the perfluorocarboxylic acids prepared was

TABLE II. FLUORINATION OF PROPIONALDEHYDE

Electricity passed: 160 amp. hr.

D_A amp./dm^2	Product obtained g.	Composition, wt. %		Yield, mol. %			Current efficiency %
		CF_3COONa	C_2F_5COONa	CF_3COONa	C_2F_5COONa	Total	
2.5	9.2	43	57	6.8	6.5	13.3	10.0
2.7	8.9	42	58	6.4	6.4	12.8	9.7
3.0	9.1	41	59	6.4	6.7	13.1	9.9
3.3	9.6	41	59	6.7	7.1	13.8	10.4
3.5	8.5	38	62	5.5	6.6	12.1	9.3

TABLE III. FLUORINATION OF BUTYRALDEHYDE

Electricity passed: 103 amp. hr.

D_A amp./dm^2	Product obtained g.	Composition, wt. %			Yield, mol. %				Current efficiency %
		CF_3COONa	C_2F_5COONa	C_3F_7COONa	CF_3COONa	C_2F_5COONa	C_3F_7COONa	Total	
2.5	2.6	23	32	45	1.3	1.3	1.4	4.0	4.6
2.7	2.8	23	31	46	1.4	1.4	1.6	4.4	5.0
3.0	2.4	23	28	49	1.2	1.0	1.4	3.6	4.3
3.3	3.1	22	28	50	1.5	1.3	1.9	4.7	5.5
3.5	3.0	19	32	49	1.2	1.5	1.8	4.5	5.3

TABLE IV. FLUORINATION OF ALDOL

Electricity passed: 154 amp. hr.

D_A amp./dm^2	Product obtained g.	Composition, wt. %			Yield, mol. %				Current efficiency %
		CF_3COONa	C_2F_5COONa	C_3F_7COONa	CF_3COONa	C_2F_5COONa	C_3F_7COONa	Total	
3.0	5.6	66	17	17	1.0	1.8	1.4	4.2	7.5
3.3	5.1	64	14	22	0.9	1.4	1.7	4.0	6.8
3.5	4.9	60	18	22	0.8	1.7	1.6	4.1	6.5

TABLE V. FLUORINATION OF PARALDEHYDE

Electricity passed: 191 amp. hr.

D_A amp./dm^2	Product obtained g.	Yield I mol. %	Yield II mol. %	Current efficiency I %	Current efficiency II %
3.0	14.4	56.1	18.7	35.4	11.8
3.3	17.5	68.1	22.7	42.9	14.3
3.5	15.7	60.9	20.3	38.7	12.9

not changed and was almost independent of the anodic current densities within the range of experimental conditions used, as was seen in the fluorination of alcohols[1)], esters[2)], ketones[3)], and unsaturated alcohols, esters and ketones[5)].

In the cold trap, about 5, 3, 1 and 1 ml. of a solution were collected at the anodic current density of 3.3 amp./dm^2 by the fluorination of acetaldehyde, propionaldehyde, butyraldehyde and aldol respectively. These solutions were identified as a mixture of fluorocarbons by their infrared absorption spectra, but they were not separated into their individual components. In the case of acetaldehyde, a considerable amount of perfluorodiethyl ether was found in the mixture.

In about 50 ml. of the residue remaining in the bottom of the cell after the distillation of hydrogen fluoride, a tarry polymeric substance was found which was soluble in such organic solvents as acetone, ethanol, ether, and carbon tetrachloride, and in hydrogen fluoride, but which was insoluble in water. This was extracted by the method described previously[5)]. In the fluorination of acetaldehyde, propionaldehyde, butyraldehyde, and aldol, 1.0, 4.3, 6.0, and 6.0 g. of the tarry substance were yielded, respectively, at the anodic current density of 3.3 amp./dm^2.

The presence of a carboxylic acid formed through acid fluoride in the residue was also identified by its formation of a sodium carboxylate (0.5$\sim$1 g.) in the same way as has been mentioned earlier[1)], and a small amount of unreacted aldehyde was identified by its formation of a 2, 4-dinitrophenylhydrazone with hydrazine in 1 : 4 hydrochloric acid solution. An examination of the formation of partially fluorinated aldehydes was attempted by the zirconium-alizarine test[6)], which was carried out after combustion treatment of the hydrazones, obtained as described above, with fused metallic potassium, but the presence of fluoride could not be confirmed. No evidence could be obtained either for the formation of perfluoroaldehydes throughout the fluorination reactions. For example, in the case of acetaldehyde, the gaseous product generated from the cell was collected in the cold trap, without bubbling through water, and the condensate was examined by its infrared absorption spectrum; however, no perfluoroacetaldehyde was found.

As a polymeric aldehyde having a six-membered oxide ring, paraldehyde was fluorinated with anodic current densities of 3.0, 3.3 and 3.5 amp./dm^2. Trifluoroacetic acid was obtained. The results are shown in Table V.

Yield I and current efficiency I were calculated in the same way as for other aldehydes, while yield II and current efficiency II were calculated on the assumption that 1 mol. of paraldehyde would give 3 mol. of sodium trifluoroacetate. The amount of fluorocarbon mixture containing perfluorodiethyl ether obtained, as in the case of acetaldehyde, was 5 ml., and the tarry polymeric substance in the residue was 1.0 g. at an anodic current density of 3.3 amp./dm^2. Although the amount of electricity required for the fluorination of paraldehyde was a little more than that for required for acetaldehyde, the overall results appeared to be similar in these two cases.

The mechanism for the formation of perfluorocarboxylic acid fluorides from aldehydes may

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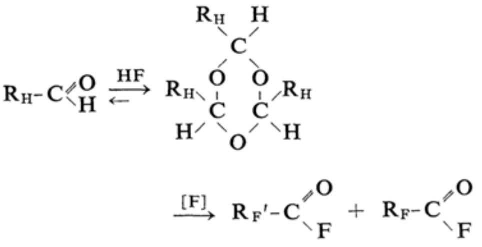
[6)] F. Feigl (Translated by R. E. Oesper), "Spot Tests", Vol. I, Elsevier Pub. Co., New York (1954), p. 252.

be explained by the following representative scheme, although the reaction could, and probably did, follow different routes simultaneously:



where R_H is the hydrocarbon radical, and R_F and $R_{F'}$ are fluorocarbon radicals.

When aldehydes are dissolved into hydrogen fluoride, they undergo rapid polymerization into para-type ringed aldehydes to reach a condition of equilibrium. The perfluorocarboxylic acid fluorides are probably formed through the process of the fluorination-fragmentation of the para-type aldehydes. The postulated mechanism should explain the bulk of the experimental evidence described above involving a low yield and a greatly degraded product of perfluorocarboxylic acids (a considerable part of which consisted of acids having a smaller number of carbon atoms than those of the starting aldehydes), the presence of a carboxylic acid fluoride in the residue, and the very similar feature fluorination reactions between acetaldehyde and paraldehyde including the formation of perfluorodiethyl ether, etc.

If alcohol has been fluorinated through the route involving the formation of intermediate aldehyde, the aldehyde thus formed would be fluorinated into acid fluoride, immediately and successively, on the surface of the electrodes, without accumulation to any considerable extent in hydrogen fluoride.

Summary

Aldehydes were fluorinated electrochemically to prepare prefluorocarboxylic acids. The results were compared with those obtained from the fluorination of alcohols, esters, ketones and unsaturated compounds.

Generally, the yield of perfluorocarboxylic acids was considerably lower in aldehydes because of a great fragmentation or polymerization in the fluorination reaction. No evidence could be obtained for the formation of a detectable amount of partially fluorinated aldehydes or perfluoroaldehydes in the reaction. The mechanism for the formation of perfluorocarboxylic acid fluorides from aldehydes was discussed.

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