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Electrochemical Fluorination of Glycols and Esters of Dicarboxylic Acids[*1]

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The electrochemical fluorination of glycols (1,3-propanediol and 1,4-butanediol), and dimethyl or diethyl esters of dicarboxylic acids (malonic, succinic, and maleic acids) was carried out. Difluoromalonic acid from esters of malonic acid, and perfluorosuccinic acid from esters of succinic acid or maleic acid, were obtained in reasonable yields, while 1,3-propanediol and 1,4-butanediol were cleaved or underwent ring formation and yielded only small amounts of perfluoro-dicarboxylic acids. Perfluoromonocarboxylic acids and fluorocarbons were among the by-products of these esters and glycols.

Alcohols and esters have been known to give perfluoro-carboxylic acid fluorides upon electrochemical fluorination.[1,2] The perfluorocarboxylic acid fluorides can be converted into the parent acids by hydrolysis. The present paper will deal with the syntheses of difluoromalonic acid and perfluorosuccinic acid by the use of this method.

Perfluoro-dicarboxylic acids have commonly been prepared by the oxidation of fluorinated cycloölefins[3-5] or diolefins.[6,7]

The oxidation of unsaturated fluoro-carboxylic acid[8] and the hydrolysis of chlorofluoro-carboxylic acid[9] have also been reported to yield perfluoro-dicarboxylic acids. The preparation of perfluorosuccinic acid from succinic acid and anhydride,[10,11] maleic acid and anhydride,[11] or from succinoyl fluoride[12] by the electrochemical process has been described.

Accordingly, glycols (1,3-propanediol and 1,4-butanediol), and dimethyl or diethyl esters of dicarboxylic acids (malonic, succinic, and

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1) S. Nagase and R. Kojima, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **64**, 1397 (1961); Japanese Pat. 417721 (1963); S. Nagase and R. Kojima, This Bulletin, **34**, 1468 (1961); Japanese Pat. 417722 (1963).

2) S. Nagase, "Fluorine Chemistry Reviews," Vol. I, ed. by P. Tarrant, Marcel Dekker, New York (1967), p. 77.

3) A. L. Henne and W. J. Zimmerschied, *J. Am. Chem. Soc.*, **69**, 281 (1947).

4) M. W. Buxton, D. W. Ingram, F. Smith, M. Stacey and J. C. Tatlow, *J. Chem. Soc.*, **1952**, 3830.

5) D. E. M. Evans and J. C. Tatlow, *ibid.*, **1954**, 3779.

6) A. L. Henne and E. G. DeWitt, *J. Am. Chem. Soc.*, **70**, 1548 (1948).

7) R. N. Haszeldine, *J. Chem. Soc.*, **1955**, 4302.

8) R. N. Haszeldine, *ibid.*, **1954**, 4026.

9) D. C. England, R. V. Lindsey, Jr., and L. R. Melby, *J. Am. Chem. Soc.*, **80**, 6442 (1958).

10) M. A. Okatov, *Khim. Nauka i Prom.*, **4**, 675 (1959).

11) S. Nagase, H. Baba, K. Tanaka and T. Abe, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **67**, 2062 (1965).

12) H. M. Scholberg and H. G. Bryce, U. S. Pat. 2717871 (1955); Japanese Pat. 221494 (1956).

maleic acids) were subjected to electrochemical fluorination. No work had previously been reported on the electrochemical fluorination of these compounds.

It was found that the esters of dicarboxylic acids afforded the expected perfluoro-dicarboxylic acids in a reasonable yield, along with degraded products, while glycols were cleaved extensively or underwent cyclization, yielding smaller amounts of perfluoro-dicarboxylic acids. Perfluoro-monocarboxylic acids and fluorocarbons, including perfluoro-ethers and bis(trifluoromethyl) peroxide, were among the by-products in these fluorination reactions.

Experimental

Materials and Apparatus. The samples subjected to fluorination were commercial-grade chemicals. Their purities were confirmed by gas chromatography.

All the features of the apparatus used for this fluorination reaction were essentially the same as those of the apparatus diagrammed in a previous paper,[11] except that a part of the electrolytic cell used was that described in another paper.[13]

Procedures. As a typical example, the procedures for the fluorination of diethyl succinate (Run 6 in Table 1) will be described. Diethyl succinate (31.4 g, 0.18 mol) was introduced into anhydrous hydrogen fluoride (1 *l*) which had been purified by electrolysis, and then the electrolysis of the solution was carried out with an anodic current density of 2.9 A/dm^2, at a cell voltage of 5—6 V and at a cell temperature of 5—6°C. The electrolysis was continued until the voltage rose to 6.8 V. The amount of electricity required for this fluorination was 191 A hr. To aid agitation, helium was introduced into the hydrogen fluoride solution at the flow rate of 15 m*l*/min from the bottom of the cell through a bubbler.

The outgoing gases, such as hydrogen, hydrogen fluoride, monobasic and dibasic perfluoro-acid fluorides, oxygen difluoride, and fluorocarbons, from the electrolytic cell were passed through the reflux condenser (kept at −15°C) into the hydrogen fluoride absorber (A), an iron tube containing sodium fluoride pellets, and the perfluoro-acid fluoride absorber (B), a pair of polyethylene bottles containing water. The gases were then led into gas-washing bottles (C), an Ichinose bottle containing an aqueous solution of sodium sulfite and sodium hydroxide with a small amount of potassium iodide, and then finally conducted into traps (D) kept in ice and liquid nitrogen.

The hydrogen fluoride in the gas stream was removed in A, perfluoro-acid fluorides were converted into the parent acids in B, oxygen difluoride and carbon dioxide were removed in C, and fluorocarbons were collected in D. The hydrogen was allowed to escape into the air.

The products in B were worked up as usual[11] to give an ether extract of perfluoro-carboxylic acids. This ether extract was dried and, after the removal of the ether, distilled under reduced pressure (20 mmHg) at a bath temperature of below 100°C. The distillate was a mixture of trifluoroacetic acid and perfluoropropionic acid, which were converted into their sodium salts (23.8 g). These were analyzed quantitatively by the base-line technique of the IR spectrum, as has previously been described in detail.[1] The composition (wt%) of the product was $CF_3COONa : C_2F_5COONa = 64 : 36$. A trace of sodium perfluorobutyrate was also present. The residue was crude perfluorosuccinic acid, which was dissolved into hot benzene; a small amount of inorganic impurity was filtered off, and the filtrate was allowed to stand overnight. The crystalline precipitate which was thus separated was recrystallized from benzene, giving white needles of perfluorosuccinic acid (5.8 g, 17.0% yield), mp 116—116.5°C (lit.[4] mp 116—116.5°C). The IR spectrum of this product was identical with that of an authentic specimen prepared by another method.[4]

Fluorocarbons (18.0 g) trapped in D were analyzed quantitatively by low-temperature distillation, gas chromatography, and IR spectroscopy, much the same methods as had been used in a series of electrochemical fluorinations of gaseous organic compounds.[14] The composition (mol%) of the fluorocarbons was as follows: carbon tetrafluoride (45.3%), fluoroform (24.2%), perfluoroethane (19.2%), perfluoropropane (3.7%), perfluorodiethyl ether (2.6%) perfluorodimethyl ether (2.2%), pentafluoroethane (1.9%), and 1,1,1,2-tetrafluoroethane (0.9%). A small quantity of unidentified compounds (0.9 g) was also found.

The experimental procedures for all the other runs, including those giving difluoromalonic acid, were similar to the one illustrated above. Difluoromalonic acid was obtained as very hygroscopic white needles, mp 117—118°C (lit.[5] mp 117—118°C) (Found: C, 25.25; H, 1.64; F, 27.0%).

Results and Discussion

The reaction conditions and the results obtained are summarized in Table 1. The product distribution of the fluorocarbon by-products obtained from five representative samples are shown in Table 2.

1,3-Propanediol was cleaved extensively into fluorocarbons and perfluoro-monocarboxylic acids, and difluoromalonic acid was produced in only a low yield. The main components of fluorocarbons were carbon tetrafluoride, perfluoroethane, and fluoroform, but perfluoropropane, perfluorodiethyl ether, perfluorodimethyl ether, perfluoro-*n*-butane, and pentafluoroethane were also formed.

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13) S. Nagase, H. Baba and T. Abe, This Bulletin, **39**, 2304 (1966).

14) Preceding paper: S. Nagase, H. Baba and T. Abe, *ibid.*, **40**, 2358 (1967).

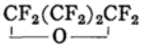
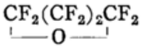
TABLE 1. FLUORINATION OF GLYCOLS AND ESTERS OF DICARBOXYLIC ACIDS[a)]

Run No.	Sample	mol	Perfluoro-dicarboxylic acid Yield %	Perfluoro-monocarboxylic acid (sodium salt) Yield%[b)] CF_3-COONa	C_2F_5-COONa	C_3F_7-COONa	Fluorocarbon g	Electricity passed A·hr
1	$HOCH_2CH_2CH_2OH$	(0.3)	$CF_2(COOH)_2$ (2.6)	10.8	10.9	—	13.6	190
2	$CH_2OH(CH_2)_2CH_2OH$	(0.18)	$(CF_2COOH)_2$ (1.8)	14.2	6.3	1.1	22.2	185
3	$CH_2(COOCH_3)_2$	(0.18)	$(CF_2COOH)_2$ (12.0)	30.5	3.1	—	5.7	136
4	$CH_2(COOC_2H_5)_2$	(0.18)	$CF_2(COOH)_2$ (11.8)	107.0	4.2	—	15.5	145
5	$(CH_2COOCH_3)_2$	(0.18)	$(CF_2COOH)_2$ (15.1)	2.2	25.3	—	10.6	152
6	$(CH_2COOC_2H_5)_2$	(0.18)	$(CF_2COOH)_2$ (17.0)	62.2	25.6	—	18.0	191
7	$(:CHCOOCH_3)_2$	(0.18)	$(CF_2COOH)_2$ (8.4)	1.5	26.1	—	14.1	147
8	$(:CHCOOC_2H_5)_2$	(0.18)	$(CF_2COOH)_2$ (9.5)	71.3	28.1	—	16.8	176

a) Anodic current density: 2.9 A/dm², Cell temperature: 5—6°C.

b) (Mole of each sodium salt obtained/mole of sample used)×100.

TABLE 2. COMPOSITION OF FLUOROCARBON PRODUCTS

Sample	Fluorocarbon mol %[a)] CF_4	CHF_3	CF_3CF_3	CHF_2CF_3	C_3F_8	n-C_4F_{10}	CF_3OCF_3	Others, %
$HOCH_2CH_2CH_2OH$	55.0	8.7	22.4	1.4	5.8	0.8	1.9	$C_2F_5OC_2F_5$ (4.0)
$CH_2OH(CH_2)_2CH_2OH$	25.3	4.9	12.7	—	16.6	2.7	0.7	 $\underbrace{CF_2(CF_2)_2CF_2}_{O}$ (37.1)
$CH_2(COOCH_3)_2$	42.4	36.6	3.0	0.4	—	—	12.5	CH_2F_2 (1.0), CF_3OOCF_3 (4.1)
$(CH_2COOCH_3)_2$	35.7	24.9	22.4	1.0	4.6	—	10.2	CH_2F_2 (1.2)
$(:CHCOOCH_3)_2$	42.7	17.1	19.6	—	16.4	0.5	3.0	 $\underbrace{CF_2(CF_2)_2CF_2}_{O}$ (0.7)

a) A small amount of unidentified products was not considered.

These compounds appeared to be derived by the fluorination reaction *via* a free-radical mechanism on the anode surface; the progressive replacement of hydrogen and some oxygen of the glycol by fluorine atoms occurred, with accompanying extensive fragmentation of the carbon skeleton due to the high reaction heat. The combination of the fragment radicals yielded perfluorodimethyl ether, perfluorodiethyl ether, and perfluoro-*n*-butane. Difluoromalonyl fluoride, which yields difluoromalonic acid by hydrolysis, may be formed through the malonyl fluoride produced by the mechanism involving fluorination, followed by dehydrofluorination at the α-carbon atoms of the glycol, much as with that of monohydric alcohols.[1)]

The electrochemical fluorination of 1,4-butanediol produced perfluorotetrahydrofuran as the principal product (23.7% yield).[*2] Perfluorosuccinic acid, perfluoro-monocarboxylic acids, and fluorocarbons were also obtained. Such cyclization reactions are often observed in the electrochemical fluorination of some oxygen-containing compounds.[15,16)] In this case, cyclization could have occurred at an early stage of the process, since the ring formation of this glycol takes place easily in acid media, and even the cyclic skeleton thus formed may be further ruptured into straight-chain fluorinated products in the fluorination. The results of the electrochemical fluorination of tetrahydrofuran (0.18 mol), which was found to afford perfluorotetrahydrofuran in a 34.7% yield, may be consistent with this interpretation.

The electrochemical fluorination of 1,2-ethanediol (0.3 mol) was examined under similar conditions. Trifluoroacetic acid was formed in a 6.1% yield, together with fluorocarbons. The fluorocarbons[*3] contained mainly carbon tetrafluoride and fluoroform. Bis(trifluoromethyl) peroxide, perfluoroethane, and perfluorodimethyl ether were also among the products.

The esters of malonic acid afforded difluoro-

[*2] 9.2 g.

15) E. A. Kauck and J. H. Simons, U. S. Pat 2644823 (1953); Brit. Pat. 718318 (1954).

16) Saline Ludwigshalle A.-G., German Pat. 1069638 (1959); Brit. Pat. 862538 (1961).

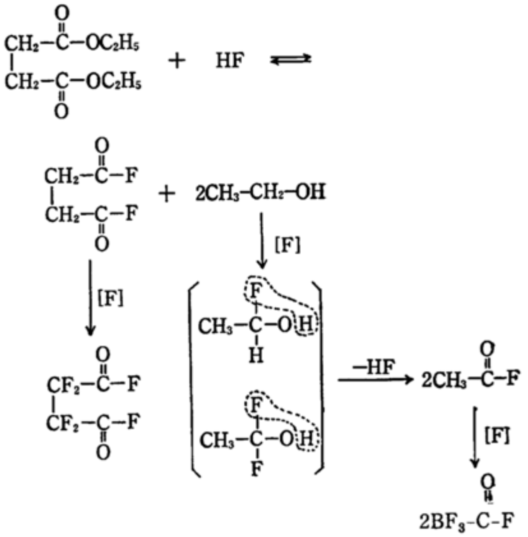
[*3] The amount of the fluorocarbon mixture was 16.5 g, but a considerable portion (4.0 g) of it went unidentified.

malonic acid in a fair yield. Perfluoropropionic acid was produced in addition to trifluoroacetic acid from these esters; both the carbonyl carbons were incorporated into the perfluoropropionic acid. The formation of a large amount of trifluoroacetic acid from the ethyl esters indicates its additional formation from the two ethoxyl groups of the ester.

For the sake of comparison, the electrochemical fluorination of free acid, malonic acid, was also performed; only traces of difluoromalonic acid and trifluoroacetic acid were yielded. The free acid was cleaved almost completely into fluorocarbons (carbon tetrafluoride, fluoroform, and methylene fluoride) and carbon dioxide in the course of the fluorination.

The esters of succinic acid and even those of maleic acid gave perfluorosuccinic acid in reasonable yields, yields which were greater than the yields from the free acids and their anhydrides.[11] Perfluoro-monocarboxylic acids and fluorocarbons, exemplified by those obtained from the methyl esters of the acids shown in Table 2, were common by-products in these fluorination reactions.

The sequence of the formation of dibasic perfluoro-acid fluorides from the esters may involve the hydrofluorolysis of the esters in hydrogen fluoride to form dibasic acid fluorides and alcohols. The alcohols formed in this way would be converted into acid fluorides through the mechanism involving fluorination, followed by dehydrofluorination, at the oxygen-bonded carbon atom.[1] Both the acid fluorides thus produced would then be fluorinated further to the corresponding perfluoroacid fluorides. For example, in the case of diethyl succinate, this reaction would be represented by the following formulae:



Although fragmentation or cyclization prevailed in the fluorination of glycols, dibasic perfluoro-acid fluorides were produced. The mechanism of the formation of dibasic perfluoro-acid fluorides from glycols could be considered to be similar to that of monohydric alcohols.[1] The production of a considerable amount of perfluorotetrahydrofuran from 1,4-butanediol shows the ease of five-membered-ring formation and the stability of an ether linkage in the fluorination reaction.