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THE ELECTROCHEMICAL PERFLUORINATION (ECPF) OF PROPANESULFONYL FLUORIDES. PART I. PREPARATION AND ECPF OF 1-PROPANESULFONYL FLUORIDE AND 1,3-PROPANEDISULFONYL DIFLUORIDE

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SUMMARY

1-Perfluoropropanesulfonyl fluoride and 1,3-perfluoropropanedisulfonyl difluoride are prepared in good yields by electrochemical perfluorination (ECPF) of 1-propanesulfonyl fluoride and 1,3-propanedisulfonyl difluoride respectively. The latter is a new compound, which could be prepared from the corresponding disulfonyl dichloride. The dependence of yield and isomerisation on temperature, starting concentration and total current are investigated. Some new partially fluorinated compounds are identified by ^{19}F NMR spectroscopy.

INTRODUCTION

First results on ECPF were published nearly forty years ago, but still nowadays results of ECPF reactions carried out in different cells are difficult to compare*. Systematic investigations concerning the influence of parameter variation have been conducted by Gambaretto et al. [2]. In the course of our work we studied the influence of temperature, starting concentration and total current on product stability and isomerisation of propane

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* For a detailed review see ref. 1

sulfonyl fluorides. Aliphatic monosulfonyl fluorides are of considerable interest because their perfluorinated derivatives have practical and technical interest. Another point is the mutual influence of two sulfonyl fluoride groups with different spacing (i.e. 1,2- or 1,3-propanedisulfonyl difluoride) on the ECPF reaction.

The above parameters cannot be varied independently of each other. Thus change in concentration varies the conductivity and with this not only current density but also reaction time and yield for volume and time. So we distinguish between independent and dependent parameters as listed in Table 1.

TABLE 1

Classification of parameters

independent	dependent
cell temperature	product yield
condenser temperature	current efficiency
starting concentration	current density
voltage	yield for volume and time
(quantity of current)	(reaction time)

Working discontinuously it is difficult to assign quantity of current and reaction time, since the reaction can be regarded to be finished, when

1. the starting material in the cell is used up

or 2. no more product is produced

or 3. the theoretical amount of current has passed.

Following (1), it is necessary to analyze the concentration of starting material in the cell in regular time intervals. In some cases the conductivity can serve as an indicator of educt concentration, provided the conductivity of reaction products is much lower than that of starting materials. But even in these cases it is very difficult to draw the correct conclusions, because conductivity decreases exponentially not linearly. So towards the end of production time current density and yield for volume and time become meaningless. The yield also decreases, since the amount of fission products increases with time.

(2) is best applicable. If at least one of the reaction products is volatile, it can be collected in outside traps. High boiling products in the cell must be analyzed quantitatively e.g. by NMR spectroscopy at appropriate time intervals.

(3) is the easiest to follow, but it depends critically on current efficiency based on current consumption according to Faraday's law. (One Faraday produces one equivalent of fluorination; one C-H replacement by C-F needs two equivalents).

These difficulties of definition play only a minor role in continous technical processes, but are very important in quantitative experiments examining the influence of the different parameters.

RESULTS AND DISCUSSION

1-Propanesulfonyl fluoride

The data in Tables 2 and 3 show a clear relation between cell temperature, reflux condenser temperature, starting concentration and product yield. Thus, increasing the values of independent parameters causes increasing yields. Most effective is a relatively high cell temperature, which on the other hand leads to a higher degree of isomerisation. These facts allow some conclusions regarding the mechanism of ECPF to be drawn:

In the strong acid $(HF)_x$ alkanesulfonyl fluorides are involved in a protonation equilibrium

$$R\text{-}SO_2F + (HF)_x \rightleftharpoons [RSO_2F\ H]^+ + [F(HF)_{x-1}]^-$$

which leads to different orientations when adsorbed on the anode. The molecule RSO_2F is adsorbed via the polar SO_2F group, the ionic species - protonated on the SO_2F groups - are adsorbed via the CH_3 (or R) group. When electrochemical oxidation takes place on the sulfonyl fluoride group C-S fission occurs SO_2F_2 and alkyl radicals being the primary products. When the alkyl group is oriented towards the anode the EC_bEC_N-mechanism as proposed by Burdon [3] and Rozhkov [4] can take place:

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}SO_2F \xrightarrow[-e]{E} \overset{+\bullet}{C}H_3\text{-}CH_2\text{-}CH_2\text{-}SO_2F \xrightarrow[-H^+]{C} \overset{\bullet}{C}H_2\text{-}CH_2\text{-}CH_2\text{-}SO_2F \quad (I)$$

$$(I) \xrightarrow[-e]{E} \overset{+}{C}H_2\text{-}CH_2\text{-}CH_2\text{-}SO_2F \xrightarrow[+F^-]{} CH_2F\text{-}CH_2\text{-}CH_2\text{-}SO_2F$$

Another possible mechanism, involving the formation of fluorine radicals,

$$F^- \xrightarrow[-e]{E} F^\bullet$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}SO_2F + F\bullet \rightarrow \overset{\bullet}{C}H_2\text{-}CH_2\text{-}CH_2\text{-}SO_2F\ (I) + HF$$

(or any other radical position)

requires a higher oxidation potential for the fluoride ion than than is required for the oxidation of carbon.

The oxidation of an alkyl group adsorbed on the anode should be regiospecific on the ω-carbon atom, while the attack of fluorine radical is not. But on the other hand the occurrence of isomerisation products shows that under the conditions of ECPF, primary radicals or carbocations undergo rearrangement reactions, thus excluding any conclusions concerning the mechanism based on partially fluorinated products.

The influence of the independent parameters can be described as follows:

Increased reflux condenser temperature allows more volatile products to escape and reduces bond fission reactions within the electrolysis cell. Loss of $(HF)_x$ limits the condenser temperature.

Increased starting concentration leads to a higher degree of adsorption, higher current density and higher yield. Moreover, the increase of concentration of reduced species must lower the redox potential according to the Nernst equation.

Increased cell temperature also gives higher yields, although the influence of a higher degree of desorption and higher redox potentials should lower the yields. It seemed, that an increasing rate of diffusion caused the improvements of the yield. In fact there is evidence that the electrode reactions are mainly diffusion controlled.

1,3-Propanedisulfonyl difluoride

As can be seen from Tables 4 and 5 this compound gave reasonable yields of 1,3-perfluoropropanedisulfonyl difluoride. The influences of cell parameters are the same as discussed before, but there are two remarkable exceptions:

1. There is no isolated migration or loss of one SO_2F group. No product can be isolated that is substituted only in 1- or 2-position. That means if there is a C-S-bond fission both SO_2F groups are lost at one time.

2. After passage of 50% of the theoretical quantity of current, no perfluorinated product can be identified in the cell.

1,3-Perfluoropropanedisulfonyl difluoride is generated in the last reaction period only. The distribution of partially fluorinated products indicates that adsorption takes place mainly in the 2-position. The degree of adsorption seems to be lower than in the case of 1-propanesulfonyl fluoride, due to the presence of two bulky SO_2F groups.

EXPERIMENTAL

^{19}F and ^{13}C NMR spectra were recorded on a BRUKER WP 80 SY (75.4 MHz). $CFCl_3$ in $CDCl_3$ was used as external standard (1.9wt%). Chemical shifts are defined negative to higher field strengths.

^{1}H NMR spectra were recorded on a JEOL PMX 60 SI with TMS as external standard.

All samples were recorded in a concentration of about 20wt% at 297 K.

List of abbreviations: d: doublet; t: triplet; q: quartet; quint: quintet; m: multiplet.

IR spectra were recorded on a Nicolet 20 DBX.

List of abbreviations: as: asymmetric; b: broad; bend: bending; m: medium; rock: rocking; s: strong; sh: shoulder; str: strech; sym: symmetrical: tw: twist: v: very; wag: wagging.

Chemical analysis was carried out on a Carlo Erba Elemental Analyser Mod. 1106.

1-Propanesulfonyl fluoride

1-Propanesulfonyl fluoride (bp. 45°C/ 13mbar) was prepared by known procedures [5,6,7]. The ^1H NMR data correspond to literature values [8,9].

^{19}F NMR: 52,64 ppm (t); $^3J_{FH}$: 3,3 Hz.

1,3-Propanedisulfonyl difluoride

1,3-Propanedisulfonyl dichloride was prepared similarly. Stoichiometric amounts of 1,3-propanedisulfonyl dichloride and KF reacted on activation with a few milliliters of 12M hydrochloric acid [10] to give the crude disulfonyl difluoride.

The solid reaction product was suspended in water and extracted with chloroform and the organic residue destilled in vacuo (bp.: 135°C/ 3mbar; mp.: 32°C; yield: 67 %).

Anal. calcd. for $C_3H_6F_2O_4S_2$:

C: 17.3% (calc.), 17.4% (found); H: 2.9% (calc.), 3.0% (found); S: 30.8% (calc.), 30.7% (found); F: 18.3% (calc.), 18.6% (found)

IR data (cm^{-1})

3072 vw; 3016 w; 2994 w (CH_2 str); 2948 w (CH_2 str); 1413 vs (SO_2 str); 1306 m; 1253 m (CH_2 wag); 1203 vs (SO_2 str); 1035 w (C-C str); 1025 w (C-C str); 849 m (CH_2 rock); 807 m (C-S str); 764 m (CH_2 rock); 726 m (C-S str); 595 m; 565 m (SO_2 rock); 490 m (CSO bend); 465 m; 402 m.

NMR data

$FO_2S-CH_2-CH_2-CH_2-SO_2F$

1 2 3

ppm	multipl.	J	Hz	assignment	nucleus
2.51	t	$^3J_{HH}$	6.3	3	^1H
3.61	m	$^3J_{HH}$	6.3	2	^1H
53.3	t	$^3J_{FH}$	4.9	1	^{19}F
18.05	t	$^1J_{CH}$	133.6	3	^{13}C
47.95	t	$^1J_{CH}$	141.7	2	^{13}C
	d	$^3J_{FC}$	18.3		

Electrochemical perfluorination reactions were carried out in a 1.1 l stainless steel cell containing cylindrical monopolar nickel electrodes with a total area of 37.6 dm^2. Teflon-spacers were used to keep the nickel cylinders in a distance of about 4 mm. The electrolyte could be drained through a ball valve in the cell bottom. Gaseous products were collected in PTFE-FEP traps kept at -78°C after passing a reflux condenser for $(HF)_x$. Current and total current were monitored, the voltage was kept constant at 7.0v. Anhydrous $(HF)_x$ was obtained by distillation, followed by preelectrolysis.

ECPF of 1-propanesulfonyl fluoride

The parameters are listed in Table 2.

After the electrolysis had been finished, the contents of the cell were isolated via the bottom valve, $(HF)_x$ was removed by distillation and the liquid residue washed with water. Volatile products were identified from the PTFE-FEP traps. Tables 3 and 6 show the identification of products and their NMR data.

TABLE 2

ECPF of $C_3H_7SO_2F$; parameters for different runs

parameters	run 1	run 2	run 3	run 4	run 5
cell temperature [°C]	0	+ 10	+ 10	+ 10	+ 10
condenser temperature [°C]	+ 10	+ 10	+ 10	0	- 20
starting concentration [mol/l]	1.0	1.0	1.92	0.5	0.5
total current [%]*	100.5	33.8**	41.2**	102.6	100.0
yield of n-$C_3F_7SO_2F$ [mol%]	13.5	30.1	40.7	41.6	13.6
current efficiency [%]	13.4	89.0	108.7	40.5	13.6
yield / volume and time [g/lh]	0.8	6.5	8.6	2.1	0.8
current density [A/dm^2]	0.30	0.34	0.36	0.23	0.23
ratio of isomerisation (n/iso)	76 : 1	27 : 1	27 : 1	23 : 1	21 : 1
reaction time [h]	41.1	11.8	22.7	24.6	21.8

* % current theoretically neccessary for 100% perfluorinated product

** Due to the rapid condensation of HF into the traps under the given conditions, the reactions were stopped.

TABLE 3

ECPF of $C_3H_7SO_2F$; composition of the trap products in %***

identified products	run 1	run 2	run 3	run 4	run 5
n-$C_3F_7SO_2F$	98.7	96.4	96.3	95.8	95.4
iso-$C_3F_7SO_2F$	1.3	3.6	3.7	4.2	4.5
C_2F_6	-	trace	trace	trace	trace
SO_2F_2	-	-	trace	trace	-

*** in relation to identified products

TABLE 4

ECPF of 1,3-$C_3H_6(SO_2F)_2$; parameters for the different runs

parameters	run 1	run 2	run 3	run 4	run 5
cell temperature [°C]	- 10	+ 10	+ 10	+ 10	+ 10
condenser temperature [°C]	- 20	- 20	+ 10	+ 10	+ 10
starting concentration [mol/l]	0.57	0.55	0.53	0.74	0.5
total current [%]*	99.2	99.2	99.2	100.4	49.6
yield of 1,3-$C_3F_7(SO_2F)_2$ [mol%]	5.4	12.8	24.2	34.0	0.0
current efficiency [%]	5.4	12.9	24.3	33.8	0.0
yield / volume and time [g/lh]	0.34	0.60	1.30	1.84	0.0
current density [A/dm^2]	0.12	0.12	0.16	0.25	0.25
ratio of isomerisation (n/iso)	-	-	-	-	-
reaction time [h]	28.0	36.9	31.5	43.1	8.3

* % current theoretically neccessary for 100% perfluorinated product

TABLE 5

ECPF of 1,3-$C_3H_6(SO_2F)_2$; composition of the products in %**

identified products	run 1	run 2	run 3	run 4	run 5
$FO_2S-(CF_2)_3-SO_2F$	12.4	32.1	53.5	46.5	0.0
$FO_2S-CH_2-CF_2-CF_2-SO_2F$	8.6	24.0	19.3	22.9	0.0
$FO_2S-CH_2-CF_2-CHF-SO_2F$	3.4	9.9	8.1	12.9	7.7
$FO_2S-CH_2-CF_2-CH_2-SO_2F$	9.5	13.0	11.9	16.0	15.2
$FO_2S-CH_2-CH_2-CF_2-SO_2F$	-	-	-	-	9.1
$FO_2S-CH_2-CHF-CH_2-SO_2F$	-	-	-	-	11.8
$FO_2S-(CH_2)_3-SO_2F$	66.0	21.1	7.2	1.7	55.4

** in relation to identified products

TABLE 6

Composition of the cell products

identified products	relative contents in mol%*
CH_2F-CHF-CH_2-SO_2F	40.2
CHF_2-CH_2-CH_2-SO_2F	27.3
CH_2F-CH_2-CHF-SO_2F	24.7
CHF_2-CHF-CH_2-SO_2F	7.8

* in relation to identified products

NMR data

CF_3-CF_2-CF_2-SO_2F
1 2 3 4

ppm	multipl.	J	Hz	assignment	nucleus
44.58	t	^4J	8.2	4	^{19}F
	t	^3J	5.7		
	q	^5J	1.3		
- 83.02	t	^4J	9.3	1	
	m		-		
-111.21	m		-	2	
-126.77	d	^3J	5.7	3	
	m		-		

ECPF of 1,3-propanedisulfonyl difluoride

The procedure was the same as described for 1-propanesulfonyl fluoride. No volatile products were collected in the PTFE-FEP traps. Tables 4 und 5 show the reaction parameters and product composition.

NMR data

$FO_2S-CF_2-CF_2-CF_2-SO_2F$
1 2 3

ppm	multipl.	J	Hz	assignment	nucleus
46.3	t	^3J	8.5	1	^{19}F
	t	^4J	3.6		
	t	^5J	3.6		
-108.7	m	n.r.*		2	
-119.5	m	n.r.		3	

$FO_2S-CF_2-CF_2-CH_2-SO_2F$
1 2 3 4

66.2	t	^4J	11.9	4	^{19}F
	m	n.r.			
45.9	t	^3J	5.7	1	
	t	^4J	8.8		
-110.8	d	^3J	5.7	2	
-111.8	d	^4J	8.8	3	
	d	^4J	11.8		
	t	$^3J_{FH}$	15.1		

$FO_2S-CHF-CF_2-CH_2-SO_2F$
1 2 3 4

65.7	t	^4J	11.9	4	^{19}F
	t	$^3J_{FH}$	4.2		
64.4	d	$^3J_{FH}$	2.0	1	
	d	^3J	7.6		
	t	^4J	11.9		
-111.5	m	n.r.		3	
-183.5	d	$^2J_{FH}$	42.6	2	
	d	^3J	7.6		
	d	^5J	1.3		
	t	^3J	12.6		

* n.r.: not resolved

$FO_2S-CH_2-CF_2-CH_2-SO_2F$

1 2 3

ppm	multipl.	J	Hz	assignment	nucleus
63.5	t	^4J	12.5	1	^{19}F
	t	$^3J_{FH}$	4.3		
-95.8	t	^4J	12.5	3	
	quint	$^3J_{FH}$	14.2		
4.53	d	$^3J_{FH}$	4.3	2	^1H
	t	$^3J_{FH}$	14.2		

$FO_2S-CF_2-CH_2-CH_2-SO_2F$

1 2 3

ppm	multipl.	J	Hz	assignment	nucleus
53.9	m	n.r.		3	^{19}F
45.7	t	^3J	5.5	1	
	t	^4J	10.0		
-109.8	d	^3J	5.5	2	

$FO_2S-CH_2-CHF-CH_2-SO_2F$

1 2 3 4

ppm	multipl.	J	Hz	assignment	nucleus
60.0	t	$^3J_{FH}$	5.5	1	^{19}F
	m	n.r.			
-180.8	t	$^3J_{FH}$	7.5	4	
3.71	d	$^3J_{FH}$	5.5	2	^1H
	d	$^3J_{HH}$	7.2		
2.49	d	$^3J_{HH}$	7.2	3	
	m	n.r.			

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