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SYNTHESIS OF PERFLUOROPROPANE-1.3-DISULFONIC ACID AND PERFLUOROBUTANE-1.4-DISULFONIC ACID *

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SUMMARY

Perfluoropropane-1.3-disulfonic acid, $HO_3S-(CF_2)_3-SO_3H$, and perfluorobutane-1.4-disulfonic acid, $HO_3S-(CF_2)_4-SO_3H$, have been prepared electrochemically from the alkanedisulfonyl difluorides. Whereas perfluoroalkanemonosulfonyl fluorides can easily be prepared via electrochemical fluorination the situation with disulfonyl difluorides is somewhat more difficult. NMR data are reported for all compounds.

INTRODUCTION

The SIMONS electrochemical fluorination process [1] is a versatile method for the preparation of perfluoroalkanesulfonic acids. Whereas the monosulfonic acids can easily be prepared [2,3], the synthesis of disulfonic acids is somewhat more difficult.

The starting material for the electrochemical fluorination is the corresponding alkanedisulfonyl difluoride, which is prepared

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* Dedicated to Prof. Dr. Friedo Huber, Dortmund, on the occasion of his 60th. birthday.

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by known methods [4,5,6]. Alkanedisulfonyl difluorides are soluble in anhydrous hydrogen fluoride and can be electrolysed in stainless steel cells with nickel electrodes under moderate conditions. Perfluorinated materials are insoluble in HF and can easily be separated.

RESULTS AND DISCUSSION

The preparation of the starting compounds started with the 1.ω-dibromoalkanes, which are converted quantitatively into the corresponding sodium sulfonates [5]. Without separating the mixture of sodium sulfonate and sodium bromide the sulfonate is chlorinated with PCl_5 [6] yielding 95 - 99 % of crude alkanedisulfonyl dichloride. By heating a mixture of alkanedisulfonyl dichloride and potassium fluoride, halogen exchange takes place [4]. The yield of raw alkanedisulfonyl difluoride is about 80 - 85 %.

Industrially available liquid hydrogen fluoride containing 1 % of water is pre-electrolysed to remove all traces of water and the alkanedisulfonyl difluoride is dissolved to a concentration of about 10 weight percent. We stopped runs after reaching the calculated amount of current based on Faraday's law. This allows us to compare the results of several electrochemical fluorination runs.

The electrochemical fluorination was done by stepwise addition of three portions of starting material to the same electrolyte. This procedure results in an increased quantity of starting material using the same amount of hydrogen fluoride as required in a batch process. Therefore the concentration of product is held in the range of 10 - 20 weight percent for a longer time, the reaction runs at an average higher current density, and the residence time of the partially fluorinated compounds in the electrolyte is increased.

The results are somewhat different from those of batch processes. In earlier work [4] our group has fluorinated propane-1.3-disulfonyl difluoride to give a mixture of perfluoropropane-1.3-disulfonyl difluoride, partially fluorinated compounds and starting material. By carrying on the process as described we have found the products to be mainly perfluoropropane-1.3-disulfonyl difluoride with only traces of partially fluorinated and starting materials, but we have also found a good quantity of volatile products like trifluoromethanesulfonyl fluoride and thionyl fluoride. Similar results were found for butane-1.4-disulfonyl difluoride.

The simple way to convert the perfluoroalkanedisulfonyl difluorides into disulfonic acids by analogy with the process used for monosulfonic acids by hydrolysing the sulfonyl fluorides with potassium hydroxide, preparing the barium sulfonates and distilling the free acids from a mixture of the barium sulfonate with oleum [3] is not applicable for disulfonic acids. There is a literature report of a process using the alkaline hydrolysis with KOH [7] followed by passage of an aqueous solution of the potassium sulfonate over a cation-exchange-column [8] to give very high yields of aqueous solutions of the acids. This procedure works well with disulfonyl difluorides to give the disulfonic acids as aqueous solutions. After removing the water the acids remain as solid hydrates containing 6 moles of water per 1 mole of disulfonic acid. These hexahydrates are stable, highly acidic and very hygroscopic compounds. Further attempts to dehydrate these compounds with trifluoroacetic acid anhydride were not successful.

EXPERIMENTAL

^{1}H and ^{19}F NMR spectra were recorded on a BRUKER WP 80 SY (80.13 MHz), ^{13}C NMR spectra on a BRUKER WM 300 (20.15 MHz). $CFCl_3$ and TMS in $CDCl_3$ were used as external reference. All samples were recorded in a concentration of about 20 wt% dissolved in water or $CDCl_3$ at 305 K. Chemical shifts are negative to higher field.

Perfluoropropane-1.3-disulfonyl difluoride, $FO_2S-(CF_2)_3-SO_2F$ (scheme 1). In a typical experiment 78.1 g (0.375 mole) propane-1.3-disulfonyl difluoride were added in three portions of 26 g to

190 g (10 mole) dried HF every time 66 % of the calculated current had been reached. The propane-1.3-disulfonyl difluoride was electrolysed at 0 °C and 5.5 V, the volatile products (19.5 g) were trapped at -78 °C. After running 121 Amphrs. (calc. 100 %) through the electrolyte the ECPF was stopped. After storage of the cell contents at -78 °C for 24 hrs. and separation of the liquid hydrogen fluoride from the solid organic material we obtained two layers of 35.3 g crude perfluoropropane-1.3-disulfonyl difluoride and 34.8 g of starting material, partially fluorinated compounds and HF. After neutralising the two layers with aqueous sodium hydrogen carbonate solution perfluoropropane-1.3-disulfonyl difluoride (b.p.: 105.5 °C, n_D^{20}: 1.3232, d_{20}: 1.786^8 g/cm^3) was obtained, yield 33.9 g (33.9 %). The second layer (5.1 g) consists of starting material containing only traces of partially fluorinated still unknown compounds.

Potassium perfluoropropane-1.3-disulfonate, $KO_3S-(CF_2)_3-SO_3K$, (n.c.). 10 g (0.032 mole) perfluoropropane-1.3-disulfonyl difluoride, 3.59 g (0.064 mole) KOH and 1.80 g (0.032 mole) CaO were refluxed in 50 ml water for 18 hrs. at 110 °C. After filtering off CaF_2, the water was distilled off and the remaining solid dried. 8.4 g (0.022 mole) potassium perfluoropropane-1.3-disulfonate (m.p.: 350 °C) were obtained (68.8 % yield).

Perfluoropropane-1.3-disulfonic acid, $HO_3S-(CF_2)_3-SO_3H$, (n.c.). 5 g (0.013 mole) potassium perfluoropropane-1.3-disulfonate dissolved in 70 ml water were passed through a cation-exchange column (Lewatit S 100, Bayer AG), the column washed until neutral, water removed from the eluate and the remaining solid dried in vacuo over P_4O_{10}. 4.48 g perfluoropropane-1.3-disulfonic acid were obtained. Titration with 0.1 M NaOH showed the presence of 6 mole water per 1 mole acid (found equiv.: 212 for the acid hexahydrate, calc. equiv.: 156 for anhydrous $HO_3S-(CF_2)_3-SO_3H$, calc. equiv.: 210 for the acid hexahydrate).

Perfluorobutane-1.4-disulfonyl difluoride, $FO_2S-(CF_2)_4-SO_2F$, (n.c., scheme 2). 72.1 g (0.325 mole) butane-1.4-disulfonyl difluoride were added in three portions of 24 g to 190 g (10 mole) pre-electrolysed anhydrous HF as described above. The electrochemical fluorination was run at 5.5 V and 0 °C. The volatile products (23.2 g) were trapped at -78 °C. After passing 139 Amphrs. (calc. 100 %) through the electrolyte the ECPF was stopped. On working up the cell contents by freezing out the organic material, two organic layers remained at room temperature after separating the HF. 33.2 g (0.091 mole) perfluorobutane-1.4-disulfonyl difluoride (b.p.: 120.0 °C, n_D^{20}: 1.3233, d_{20}: 1.820^0 g/cm^3) were obtained (28 % yield). The second layer (7.0 g) consists of starting material and traces of partially fluorinated still unknown compounds.

Potassium perfluorobutane-1.4-disulfonate, $KO_3S-(CF_2)_4-SO_3K$, (n.c.). 10 g (0.027 mole) perfluorobutane-1.4-disulfonyl difluoride, 3.06 g (0.055 mole) KOH and 1.53 g (0.027 mole) CaO were refluxed in 60 ml water for 20 hrs. at 110 °C. After filtering off CaF_2, the water was distilled off and the remaining solid was dried. 10.4 g (0.024 mole) potassium perfluorobutane-1.4-disulfonate (m.p.: 235 °C) were obtained (89 % yield).

Perfluorobutane-1.4-disulfonic acid, $HO_3S-(CF_2)_4-SO_3H$, (n.c.). 9.3 g (0.021 mole) potassium perfluorobutane-1.4-disulfonate dissolved in 100 ml water were passed through a cation-exchange column (Lewatit S 100, Bayer AG) and the column washed until neutral. After distilling off the water, the remaining solid was dried in vacuo over P_4O_{10}. 7.65 g perfluorobutane-1.4-disulfonic acid were obtained. Titration with 0.1 M NaOH showed the presence of 6 mole water per 1 mole acid (found equiv.: 236 for the acid hexahydrate, calc. equiv.: 181 for anhydrous $HO_3S-(CF_2)_4-SO_3H$, calc. equiv.: 235 for the acid hexahydrate).

starting materials	propane-1.3-disulfonyl difluoride	78.1 g
	hydrogen fluoride	190 g
yield	cell contents (organics + HF)	156.8 g
	trap contents	19.5 g

cell temperature	0 °C
condenser temperature	-20 °C
starting concentration	13.7 wt%
cell voltage	5.5 V
total current	100.0 %
current efficiency	33.9 %

identified compounds in cell:

perfluoropropane-1.3-disulfonyl difluoride	33.9 g
educt and partially fluorinated compounds	5.1 g
perfluorinated cracking products	traces

identified compounds in trap:

perfluoropropane	traces
perfluoromethanesulfonyl fluoride	11 %
perfluoroethanesulfonyl fluoride	9 %
thionyl fluoride	13 %
sulfuryl fluoride	11 %
hydrogen fluoride	56 %

Scheme 1. Electrochemical perfluorination of propane-1.3-disulfonyl difluoride

starting materials	butane-1.4-disulfonyl difluoride	72.1 g
	hydrogen fluoride	190 g
yield	cell contents (organics + HF)	115.0 g
	trap contents	23.2 g

cell temperature	0 °C
condenser temperature	-20 °C
starting concentration	12.6 %
cell voltage	5.5 V
total current	100.0 %
current efficiency	28 %

identified compounds in cell:

perfluorobutane-1.4-disulfonyl difluoride	33.2 g
educt and partially fluorinated compounds	7.0 g
perfluorinated cracking products	traces

identified compounds in trap:

trifluoromethane	traces
perfluorobutane	traces
perfluoromethanesulfonyl fluoride	8 %
perfluoroethanesulfonyl fluoride	11 %
perfluorobutane-1-sulfonyl fluoride	12 %
thionyl fluoride	12 %
sulfuryl fluoride	9 %
sulfur tetrafluoride	traces
hydrogen fluoride	48 %

Scheme 2. Electrochemical perfluorination of butane-1.4-disulfonyl difluoride

	(Br	– $CH_2)_2$	– CH_2		(Br	– CH_2	– $CH_2)_2$
^{1}H		3.9	2.7	^{1}H		3.4	2.0
^{13}C		34.5	31.0	^{13}C		32.3	30.6
	(NaO_3S	– $CH_2)_2$	– CH_2		(NaO_3S	– CH_2	– $CH_2)_2$
^{1}H		3.2	2.4	^{1}H		3.6	4.5
^{13}C		49.5	20.0	^{13}C		52.7	25.3
	(ClO_2S	– $CH_2)_2$	– CH_2		(ClO_2S	– CH_2	– $CH_2)_2$
^{1}H		3.9	2.8	^{1}H		3.8	2.3
^{13}C		61.3	19.4	^{13}C		63.5	22.0
	(FO_2S	– $CH_2)_2$	– CH_2		(FO_2S	– CH_2	– $CH_2)_2$
^{1}H		3.6	2.6	^{1}H		3.4	2.1
^{19}F	54.4			^{19}F	54.2		
^{13}C		47.6	17.8	^{13}C		49.8	21.3
	(FO_2S	– $CF_2)_2$	– CF_2		(FO_2S	– CF_2	– $CF_2)_2$
^{19}F	47.1	-108.1	-119.0	^{19}F	46.8	-108.2	-120.1
^{13}C		114.7	109.8	^{13}C		114.7	110.3
	(KO_3S	– $CF_2)_2$	– CF_2		(KO_3S	– CF_2	– $CF_2)_2$
^{19}F		-115.7	-121.3	^{19}F		-113.5	-119.8
^{13}C		117.1	114.1	^{13}C		116.8	114.3
	(HO_3S	– $CF_2)_2$	– $CF_2^{*)}$		(HO_3S	– CF_2	– $CF_2)_2^{*)}$
^{1}H	10.3			^{1}H	10.6		
^{19}F		-113.3	-118.7	^{19}F		-113.7	-119.8

Scheme 3. NMR data of propane-1.3- and butane-1.4-derivatives (all chemical shifts are given in ppm, *: acid hexahydrate)

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