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CURRENT BALANCE OF THE ELECTROCHEMICAL FLUORINATION OF A TRIALKYLAMINE

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SUMMARY

The electrochemical fluorination of dibutylmethylamine was studied. All the fluorination products formed, liquid, gaseous, and dissolved in HF, and also the hydrogen evolved were quantitatively determined. From either their formulae or their relative fluorine contents the amount of current necessary for their formation was estimated. Altogether, the fluorination products determined cover about 86 - 92 % of the current applied. A major part of the current was consumed by production of polyfluorinated compounds, which remained dissolved in the hydrogen fluoride.

INTRODUCTION

The electrochemical fluorination (ECF) (following Sartori's [1] proposal, the SIMONS-process should be called more precisely 'electrochemical perfluorination') was designated as a comparatively mild perfluorination method, yielding saturated compounds with all the hydrogen replaced by fluorine and with functional groups and original carbon skeleton often preserved. By-products should nearly exclusively stem from carbon-carbon or carbon-heteroatom cleavages [2, 3, 4]. Contrary to this description, the occurrence of hydrogen-containing polyfluorinated compounds as impurities in the crude fluorination products is a well known problem [5]. In few cases these compounds were studied in detail [5, 6, 7, 8]. In their investigations of the ECF mechanism

Gambaretto and co-workers [6] have demonstrated the formation of derivatives of comparatively low fluorine content dissolved in the hydrogen fluoride. These studies were carried out with very highly concentrated N-methylmorpholine solutions. The improvement of the yield by application of used HF for a new ECF experiment, as claimed by Wechsberg [9] for production of F-alkanesulphonyl fluorides, can be seen as an evidence for the occurrence of intermediates dissolved in HF. Such intermediates, as definite stages of the perfluorination reaction, would be in contradiction to the widely accepted mechanism according to which a substrate molecule has to be adsorbed at the anode to become fluorinated and will be released from the anode only after being completely fluorinated [3, 10].

However, the majority of the investigators are only interested in perfluoro products and have not studied partially fluorinated ECF products. Consequently, as far as we know, no total mass and current balance has been reported. Therefore, attempts have been made by us, to determine quantitatively all the products, liquid, gaseous, and dissolved in HF, which are formed during electrofluorination of tertiary amines. Here we report the first results of these studies.

RESULTS AND DISCUSSION

Experimental data and operation conditions are stated in Table 1. One can see that the amount of hydrogen formed at the cathodes during ECF of dibutylmethylamine (DBMA) is equivalent to about 86 % of the amount of electric current consumed. This value corresponds with current efficiencies of 90 % and 95 % for electrolytic fluorine production as given by Conte et al. [11] and Rudge [12], respectively. As with fluorine cells, losses in efficiency could result from HF-reformation. The current efficiency of the hydrogen liberation was taken as a basis for the calculations of theoretical current requirements for the formation of fluorinated compounds.

The anodically formed fluorination products are divided among 'perfluorinated' liquid phase (crude product of ECF), gaseous phase, and HF-phase in comparable extent (Table 1).

The liquid crude product is a mixture consisting mainly of perfluoro dibutylmethylamine (FDBMA), other perfluoro amines derived from DBMA by carbon-carbon cleavage or by ring formation, and polyfluorinated amines with one - or less frequently more - hydrogen atoms per molecule. For current balance calculations the whole mixture is taken into account as FDBMA. The error of this simplification is acceptable for the purpose of estimating necessary current amounts by eqn. 1 (p. 8). The amount of current required for the formation of the liquid fluorination products (crude perfluorinated amine) counts for about one third (35 %, 35 %, and 27 %, respectively) of the current applied. This is within the range of yields often reported for ECF of tertiary amines.

The gaseous products from the ECF-cells consisted mainly - after removal of HF - of cathodically produced hydrogen and partially of low-boiling fluorination products. The latter are NF_3, CF_4, C_2F_6, C_3F_8, C_4F_{10}, and c-C_4F_8. They were detected and identified by GC-, GC/MS- and IR-analysis, respectively, and their amounts were determined by GC as well as volumetric (sum of all) (Table 1). These compounds stem from fragmentations of DBMA. Therefore, for one mole NF_3, resulting from total fragmentation, 9 mole carbon atoms should be liberated in form of gaseous C-F-compounds. Additional gaseous compounds ought to be produced in connection with the formation of e.g. $(C_4F_9)(C_3F_7)NCF_3$. Thus a C:N-ratio of 9:1 or even higher was to be expected. The experimental ratio (from Table 1) is somewhat lower (3.7:1; 4.9:1; but 10.3:1), probably due to analytical inaccuracies. Altogether, the gaseous fluorination products cover about one fourth (24.7 %, 24.7 %, 29.4 %) of the consumed current. (A projection of the NF_3-values on the basis N:C equal to 1:9 results in higher figures for the necessary current.) Abe *et al.* in their paper about the ECF of N,N-dimethylalkylamines and N,N-dialkylmethylamines [7] reported detailed values from which one can calculate that liquid and gaseous fluorination products together count for about 22 % to 45 % of the current applied, with the low-boiling fluorocarbons covering only about 4 % to 10 % of the current. These values are considerably lower than ours, possibly due to insufficient condensation of the gases (trap cooled with dry ice/acetone only).

TABLE 1

Experimental conditions and results of dibutylmethylamine - ECF

Experimental conditions		Run I	Run II	Run III
volume of ECF-cell	[ml]	1600	1600	450
amount of HF	[g]	1257	1120	333
amount of H-DBMA	[g]	143	280	78
	[%]	10.2	20	19
amount of current (Q) theoretical required (E = 1.0) for ECF of the amine	[Ah]	1126	2204	614
ECF-voltage	[V]	6-8	6-8	5-8
ECF-current	[A]	10	10	20
current density	[A/dm²]	2.5	2.5	5
amount of current (Q) applied	[Ah]	1000	2000	490
ECF-results				
H_2 evolved	[l]	364	677	185
current efficiency (E) for H_2-formation		0.87	0.81	0.90
liquid fluorination products	[g]	140	265	56
Q (required)^1	[Ah]	348	707	134

gaseous fluorination products[2]				
NF_3	[l]	6.8	10	1.8
CF_4	[l]	13.9	20	2.8
C_2F_6(+CHF_3, CH_2F_2)	[l]	1.8	4	0.5
C_3F_8+C_4F_{10}(c-C_4F_8)	[l]	2.5	6.8	3.7+0.9
Q (required)[3] (sum of all)	[Ah]	235	455	132
oxidizing agents (calc. as Mol F•)		0.4	1.2	0.4
Q (required)	[Ah]	12.3	39.7	11.9
fluorination products dissolved in HF	[g]	210	300	120
fluorine content (F)	[%]	48	49	43
Q (required)[4]	[Ah]	327	512	162
fluorination products totally; Q (requ.)	[Ah]	922.3	1713.7	439.9
part of the applied current covered by the determined fluorination products	[%]	92	85.7	89.8

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[1] calculated according to Eq. 1; all liquid products taken as FDBMA

[2] from GC-analysis of total gas stream

[3] calculated according to Eq. 1; values for H and B, respectively, were taken as follows: NF_3 0/3; CF_4 3/1; C_2F_6 4.5/1.5; C_3F_8 6/2; C_4F_{10} 9/1

[4] calculated according to Eqn. 2

After electrolysis the hydrogen fluoride contained considerable amounts of organic material which is different from the starting amine (Table 1). This material is a complex mixture with a rather high average fluorine content of 43 % to 49 % (for comparison: FDBMA F = 76.6 %). (Results of analytical investigations are subject of a separate paper which is being prepared.) It contains no perfluoroamine, in agreement with the findings of Abe et al. [7]. These polyfluorinated compounds dissolved in HF count for about one third of the total current (32.7 %, 25.6 %, 33.1 %), calculated according to Eqn. 2 (p. 8).

All determined fluorination products together cover about 89 % (92 %, 85.7 %, 89.8 %) of the amount of current applied. For the three different groups, liquid fluorination products, gaseous fragmentation products and polyfluorinated dissolved products, the reliability of their quantitative analysis is lowest in case of gaseous products, where some losses might have occurred. Therefore, one may say that each of these groups had consumed roughly one third of the total current.

The occurrence of large amounts of polyfluorinated compound dissolved in HF is not at all linked with ECF of dibutylmethylamine or with trialkylamines only [5]. On the contrary we found it is a normal part of all electrochemical fluorination reactions carried out in our laboratory. Sometimes, partially fluorinated compounds became the major product with nearly no perfluorination products. From the point of view of "normal" electrochemical fluorination they are more or less unavoidable by-products. However, we have been starting investigations with the aim to explain their role in ECF-mechanism and to make use of them in further reactions, including attempts to perfluorinate them. The results of some of these investigations, which are still in progress, will be presented in the following paper.

EXPERIMENTAL

Electrochemical fluorination reactions

The electrochemical fluorination reactions were carried out in the manner originally developed by Simons [13]. Two cells of different volumes (1600 ml and 450 ml, respectively) but with equal equipment were used. Each cell was fitted with a bottom valve for liquids, a reflux condenser (at -20 °C), an electrode package of 4 anodes (total area 4 dm^2) and 5 cathodes, made from nickel and arranged alternatively with a distance of 4.5 mm each, and with a HF-level indication device.

The gas stream from each cell was passed through the reflux condenser, a KOH/KI-solution, conc. H_2SO_4, a cooling trap at -78 °C, a second cooling trap at -196 °C, a tube with $CaCl_2$ and was then caught pneumatically over water. The electrochemical fluorinations were carried out at temperatures between 5° and 15 °C, at 5 - 8 V and with 10 A and 20 A, respectively (Table 1).

Analysis of ECF products

Samples of the gas stream were taken every 10 Ah by a syringe through a septum before the first cooling trap. The relative portions of the gaseous species were determined by GC, using authentic samples for calibration. Their total amounts were pneumatically determined, i.e. the volume of hydrogen could be measured exclusively by maintaining the second cooling trap at -196 °C (as proved by GC), and the sum of all gaseous species was determined after evaporating the products condensed in the cooling traps.

Liquid perfluorination products were analyzed by GLC and their fluorine content determined by the WICKBOLDT-method [14]. The working up procedure for the HF-phase was as follows: A weighed sample (about 20 g) was warmed to room temperature. To the residue NaOH and water were added to a pH of about 12. The liquid products (organic mixture and aqueous solution) were separated from the solid salts formed and the latter extracted with 3 portions of diethylether of about 50 ml each. The aqueous phase was separated from the organic ones and also extracted with ether (3 x 50 ml). All organic phases were combined and the ether under vacuum removed. The remaining dark-brown coloured liquid was weighed and its fluorine content determined.

Estimation of theoretical current consumption

The amount of current required for the formation of the different types of fluorination products was calculated as follows:

$$Q = (2H+B) \times {}^{1}/E \times {}^{m}/M \times 26.8 \quad [Ah] \qquad (1)$$

where:

Q = amount of current required, given in ampere-hours

H = number of hydrogen atoms replaced by fluorine

B = number of carbon-carbon or carbon-nitrogen bonds to be split

E = current efficiency, derived from hydrogen liberation (see RESULTS and DISCUSSION, Table 1)

m = actual mass (grammes) of fluorination product

M = molecular weight of fluorination product

In case of the complex mixtures of partially fluorinated compounds isolated from the HF, where neither all the individual species nor their respective amounts were known, a summary calculation was used:

$$Q = \frac{mF}{100 \times 19} \times 2 \times 26.8 \times {}^{1}/E \quad [Ah] \qquad (2)$$

where:

Q, m, E as above

F = percentage of fluorine in the sample.

The derivation and the use of these equations is shown by the following two examples.

Example 1: Formation of CF_4 from DBMA

Summary equations

a) $\geq N-(C_3H_6)-CH_3 + 6F^- \xrightarrow{-6e^-} \geq N-(C_3H_6)-CF_3 + 3HF$

b) $\geq N-(C_3H_6)-CF_3 + F^- \xrightarrow{-e^-} \geq N-(C_3H_6)^{\cdot} + \underline{CF_4}$

This way 3 hydrogen atoms are replaced by fluorine (<u>i.e.</u> $H = 3$ in Eqn. 1) and one carbon-carbon bond is splitted ($B = 1$ in Eqn.

1). The replacement of one hydrogen atom by fluorine requires 2 Faraday (2 x 26.8 Ah), but those of a carbon atom only 1 Faraday per mole fluorination product. Thus the formation of 78.6 g (20 l) CF_4 (average current efficiency 0.81, see Table 1, Run II) needs

$$Q = (2\times3+1) \times {}^{1}/0.81 \times {}^{78.6}/88 \times 26.8 = 206.9 \text{ Ah.}$$

Example 2: Formation of partially fluorinated products
For simplification, all fluorine in these compounds is regarded as being the result of hydrogen replacement. Consequently, for each mole of fluorine (calculated from the mass of the sample and its fluorine content) are theoretical 2 Faraday needed (the actual value has to be corrected by the average current efficiency). The formation of 210 g product with 48 % F (average current efficiency 0.87, see Table 1, Run I) needs

$$Q = \frac{210\times48}{100\times19} \times 2 \times 26.8 \times {}^{1}/0.87 = 326.9 \text{ Ah.}$$

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