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ON POLYFLUORINATED, HF SOLUBLE COMPOUNDS FORMED DURING THE ELECTROCHEMICAL FLUORINATION OF DIBUTYLMETHYLAMINE*

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SUMMARY

The electrochemical fluorination of dibutylmethylamine yields, besides other products, considerable amounts of polyfluorinated compounds which remain dissolved in HF. Since the occurrence of such compounds is a widespread phenomenon in ECF, their formation as well as their composition was studied. Whereas some partially fluorinated compounds are likely to be intermediates in the fluorination process, others remain inert toward further ECF. The latter have on average about 9 of the 21 H-atoms replaced by F, with almost no F at C-atoms adjacent to the N-atom.

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*Dedicated to Professor L. Kolditz on the occasion of his 60th birthday.

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INTRODUCTION

The occurrence of incompletely fluorinated by-products during any ECF experiment is a well-known phenomenon [1,2,3]. In the previous paper [4] we showed that the partially fluorinated or polyfluorinated compounds, which remain dissolved in HF, consumed as much electric current for their formation as the perfluorinated products did. The occurrence of such a major (sometimes even dominant) group of polyfluorinated compounds leads to the following questions: Do polyfluorinated compounds play a role in ECF-perfluorination? Are the polyfluorinated compounds only unreactive by-products? What prevents them from becoming perfluorinated? At which time of the ECF-experiment are they formed? What is their reactivity? What types of compounds are these polyfluorinated compounds? In this paper we try to give some answers based on experimental studies of the ECF of dibutylmethylamine (DBMA).

RESULTS AND DISCUSSION

All ECF experiments with dibutylmethylamine (DBMA) yielded considerable amounts of polyfluorinated products which remained dissolved in the hydrogen fluoride (these products are subsequently called 'HF-phase') [4]. The fluorine content of the HF-phase reached about 52 % on average at the end of the ECF experiments, corresponding to the formula $C_9H_{13}F_8N$. The mean molecular weight was in the range from 300 to 320, corresponding to $C_9H_{12}F_9N$ and $C_9H_{11}F_{10}N$, respectively. To get some insight into the kinetics of their formation, we studied the occurrence of polyfluorinated compounds as well as the drop in DBMA concentration in the course of ECF. In Fig. 1 the relative content of unreacted DBMA in the mixture of organic compounds isolated from the HF (i.e. from the HF-phase) is plotted against the applied current. One can see that the DBMA concentration drops rapidly. The initial DBMA decrease is much faster than explainable by assuming that only perfluorination reactions can take place. That implies that first of all most of the DBMA is only partially

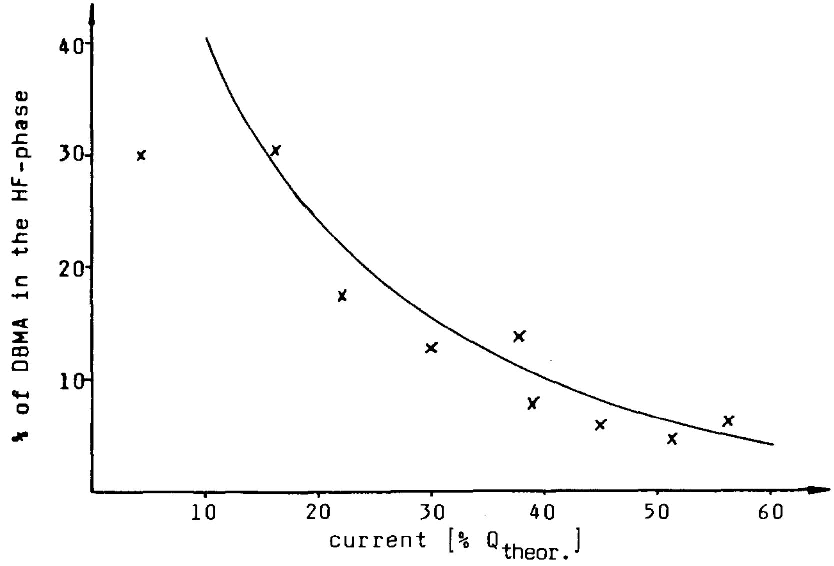


Fig. 1. Relative amount of unreacted DBMA in the HF-phase as a function of the applied current.

fluorinated, thereby consuming small amounts of current per mole of amine. The occurrence of a variety of partially fluorinated compounds is proved by GC and by ^{19}F-NMR. Accordingly, the perfluorinated amine FDBMA is most probably formed by extensive fluorination of pre-formed partially fluorinated compounds, and not (or not only) by a 'zipper-mechanism' [5]. These findings are in agreement with the proposals made by Plashkin et al. [6] who studied the ECF of dialkylanilines.

While these experimental data give evidence for the role of polyfluorinated compounds as intermediates in the perfluorination reaction, the large amount of the polyfluorinated HF-phase at the end of an ECF experiment needs an explanation. Obviously, the HF-phase resists perfluorination under the given experimental conditions. This resistance against perfluorination is a property of the compounds rather than the result of a kind of electrode-poisoning. Attempts to perfluorinate the HF-phase by transferring it into a new ECF cell failed. Since, normally, the use of partially fluorinated compounds for ECF is regarded as advantageous [7,8], the inertness of the HF-phase was unexpected. Considerations to explain the low reactivity by assuming

steric shielding of the hydrogen atoms by the fluorine atoms (as proposed for other compounds [9]) have no real basis because of the low average number of fluorine atoms per molecule.
Thus, a more detailed analysis of the HF-phase is necessary to shed some light on the question why some partially fluorinated compounds become perfluorinated during ECF whilst others remain unreactive.

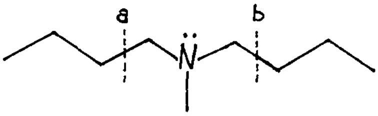
GC analysis of HF-phases showed them to be very complex, even shortly after the electrolysis was started, with more than 100 compounds detectable at the end of the ECF experiments. Therefore, we did not try to isolate compounds from HF-phases, but studied the complete mixtures by ^{19}F-NMR and GC/MS, respectively. NMR-spectra of the HF-phases were recorded in the course of batch-like ECF experiments as well as of semi-continuous ECF experiments. From one HF-phase, isolated shortly before the end of a batch-experiment, a GC/MS-analysis was done.

Prior to the discussion of the analytical data, some basic considerations are necessary. In an ECF experiment there are two different liquid phases among which partially fluorinated compounds can be distributed. These are the nonpolar perfluorocarbon liquid and the polar, strongly acidic hydrogen fluoride, respectively. The majority of the partially fluorinated compounds, quantitatively as well as qualitatively, remains in the hydrogen fluoride. These compounds of the HF-phase are nearly insoluble in FDBMA, and, vice versa, the incompletely fluorinated constituents of the crude perfluorocarbon are nearly insoluble in HF, as could be proved experimentally. From this follows that the compounds of the HF-phase exhibit a certain basicity, in contrast to the partially fluorinated compounds dissolved in FDBMA. As a consequence, compounds of the type $(R_{H,F}CF_2)_2NCF_3$ are not likely to occur in the HF-phase.

Starting from these considerations the GC/MS and the ^{19}F-NMR data will be discussed.

GC/MS

The sample for GC/MS-analysis was taken from an HF-phase of an ECF batch-experiment shortly before the electrolysis came to an end. Thus, the sample is very likely to contain, nearly exclusively, unreactive polyfluorinated compounds. Altogether, this HF-phase consists of at least 100 different compounds; the gas-chromatogram from the GC/MS machine is shown in Fig. 2. From these compounds mass spectra were recorded, using electron impact ionization and in addition chemical ionization, which allows a better identification of the molecular weight by the $[M+1]^+$ peaks. The interpretation of the fragmentation patterns, obtained by using electron impact ionization, started from the following assumptions: Fragmentation of tertiary amines occurs preferably as a β-cleavage like



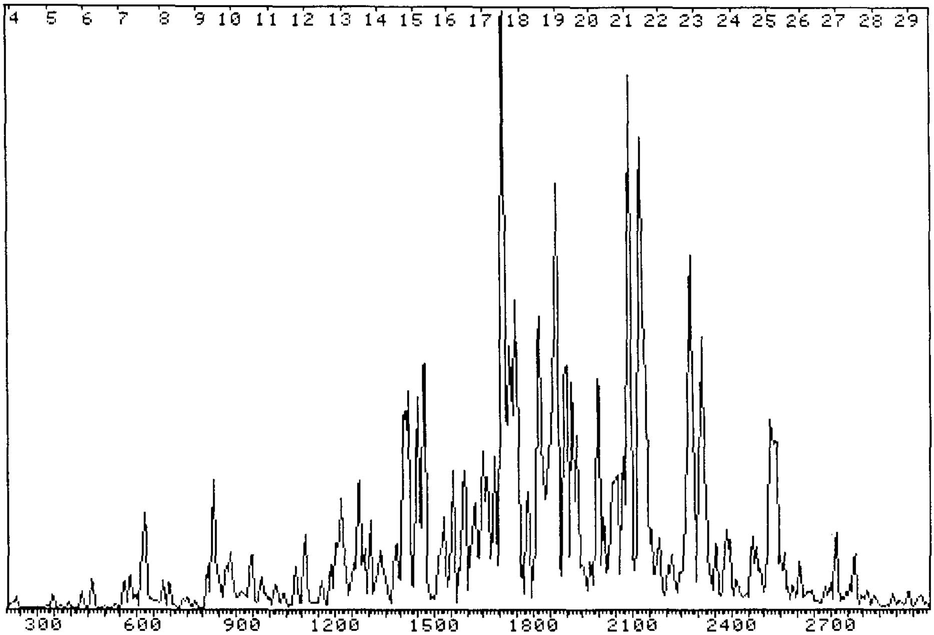


Fig. 2. Gas-chromatogram of the HF-phase from the GC/MS-analysis.

where the cleavage might take place at either a or b. The resulting ion will be stabilized by the free electron pair at the nitrogen, therefore, this fragment is dominating. Knowing the molecular weight from the $[M]^{+\cdot}$ peak the number of fluorine atoms in the molecule can be determined. If, additionally, the $^m/e$-values of the corresponding ions from the β-cleavages are known, it is also possible to calculate the distribution of the fluorine atoms within certain limits. Two examples may demonstrate the way (see Fig. 3): Compound A gives a molecular ion peak at $^m/e$ 305, with $[M-H]^+$ at $^m/e$ 304 and $[M-F]^+$ at $^m/e$ 286, and two intense peaks at $^m/e$ 190 (base peak) and $^m/e$ 172, respectively. The calculation of the elemental compositions gives $C_9H_{12}F_9N$ for $^m/e$ 305, $C_6H_9F_5N$ for $^m/e$ 190 and $C_6H_{10}F_4N$ for $^m/e$ 172. Thus, the sum of fluorine atoms in the β-cleavage products ($^m/e$ 190 and $^m/e$ 172) is equal to the number of fluorine atoms in the molecule. That means, no fluorine is bound to one of the three α-carbon atoms. If, however, one or more fluorine atoms were bound to α-carbon, the sum of the fluorine atoms in β-cleavage products will exceed the number of fluorine atoms in the molecule to a corresponding extent. For compound B a fluorine content of eight atoms can be calculated from the mole peak at $^m/e$ 287. The β-

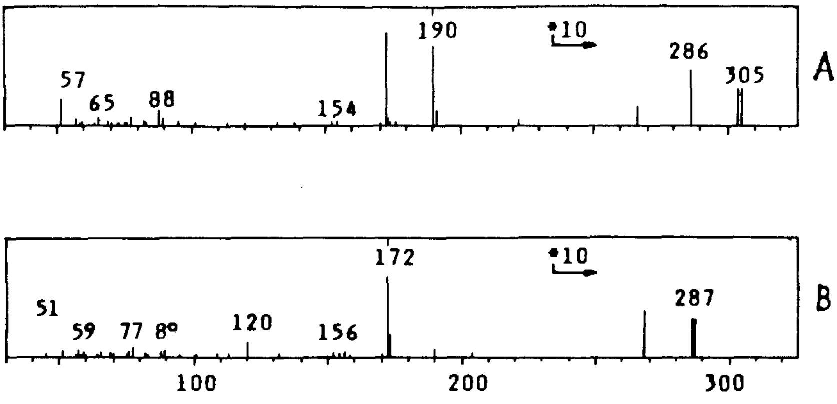


Fig. 3. Mass spectral data for two chromatographic peaks from the HF phase.
*10 = 10-fold amplification

cleavage results in only one intense peak (base peak) at $^m/e$ 172. This indicates that four fluorine atoms are situated at each of the two n-butyl-groups, again with no fluorine bound to an α-carbon.

The following MS results are based on the evaluation of the majority of the GC-peaks, corresponding to 90.3 % of the total ion response of the GC/MS-run of the HF-phase. Nearly all identified compounds are of the di-n-butyl-methyl-amine type. Only traces of compounds like butyldimethyl-, butylethylmethyl- and butylpropylmethylamine could be observed. The polyfluorinated compounds of the type $C_9H_nF_mN$ (with n + m = 21) have from 7 to 12 F-atoms per molecule, mostly 9 F-atoms, as shown in Table 1. From the values in Table 1 one can calculate the mean composition as $C_9H_{11.8}F_{9.2}N$ (equal to 56.6 % F-content). The distribution of F-atoms within the molecules is shown in Table 2. One can see that there are only very few compounds with one or two F at α-C-atoms, the majority has no F-atoms there. Furthermore, the F-atoms are mostly as symmetrically distributed among the two butyl groups as possible (a = b or a = b + 1, see Table 2).

TABLE 1

Occurrence of partially fluorinated dibutylmethylamines $C_9H_nF_mN$ (n + m = 21) in the HF-phase

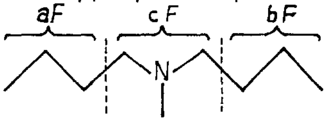
$[M]^{+\cdot}$	m	n	% of the total ion response
269	7	14	1.0
287	8	13	19.4
305	9	12	42.4
323	10	11	17.9
342	11	10	8.0
360	12	9	1.6
		total	90.3

TABLE 2

Distribution of F-atoms in the polyfluorinated dibutylmethylamines $C_9H_nF_mN$ of the HF-phase

Type	% of total ion response
a = b or a = b + 1; c = o	85.3
a = b + 2; c = o	3.4
c = 1 or c = 2	1.7
total	90.4

a, b, c = number of F-atoms in the appropriate parts of the molecules, according to



These results from GC/MS-analysis are in good agreement with the considerations discussed above. The mean F-content of the HF-phase (56.6 %), calculated from the mass spectra, corresponds within acceptable limits with the experimental value (52 %). Furthermore the spectra confirm the consideration that the α-C-atoms cannot be completely fluorinated. However, two results were not expected, these are the nearly complete absence of F on the α-C-atoms and the almost exclusive occurrence of compounds having the carbon-skeleton of DBMA.

^{19}F-NMR

Supplemental analytical information can be derived from ^{19}F-NMR-spectra of the HF-phase. All these spectra are very complex with no single compound detectable. Consequently, it is only possible to try to co-ordinate the main signals with particular groups and to evaluate their changes during ECF. These substantial changes are the most remarkable results of the NMR analysis. A comparison of the ^{19}F-NMR-spectra taken in the course of batchwise ECF-experiments as well as of semi-continuous experiments shows at least three types of signals. They differ from each other in their relative intensity with proceeding ECF. Firstly, there are signals which increase in intensity, and belong to polyfluorinated compounds of low reactivity, the concentration of which increases with proceeding electrolysis. Signals of this type are at about 80 ppm, at 131 - 138 ppm, and also at about 74 ppm, the latter being more important in the semi-continuous experiments. Secondly, there are signals with a nearly constant and moderate intensity. These belong partly to intermediates which are formed and consumed at about the same rate and partly to the unreactive by-products. Signals of this type are at about 60 ppm, 85 ppm, 100 ppm, at 117 - 125 ppm, and at 190 - 220 ppm. Finally, for signals of a third type, the intensity decreases with proceeding electrolysis. Some have initially a moderate to low intensity which finally decreases (this can be found in the semi-continuous experiments especially), e.g. at about 64 ppm, 184 ppm and at 230 - 242 ppm. These belong to intermediates of the ECF reaction. Additionally, there are signals which appear with high intensity shortly after the start of the electrolysis, but decrease or even disappear very rapidly with proceeding electrolysis. These are at about 89 ppm, 116 ppm and 173 ppm. Surprisingly, they could also be observed under semi-continuous conditions. Since under these conditions intermediates can be produced at all times, the rapidly disappearing signals cannot belong to them. The assumption that these signals stem from compounds which, with the beginning of perfluorocarbon production, become dissolved in the perfluorocarbon phase is also unlikely, since they do not occur in ^{19}F-NMR-spectra of crude FDBMA. On the basis of the available experimental results no definite assignation is possible.

An evaluation of all the ^{19}F-NMR-data of the HF-phase from DBMA electrofluorination leads to the following results: 1) The NMR-analysis confirms that partially fluorinated compounds play a role as intermediates in the ECF. This means also that the 'zipper-mechanism' cannot be the only one. 2) ECF is linked with the formation of partially fluorinated by-products, but there is no evidence for the occurrence of highly fluorinated compounds dissolved in the HF (e.g. with one or two H-atoms per molecule as they can be found in crude FDBMA [Groß, Dimitrov and Rüdiger, unpublished; see also 3]). Neither is there an indication of compounds having α-carbon atoms completely fluorinated, on the contrary, compounds having the terminal C-atoms of the n-butyl groups fluorinated are very likely (on the basis of the following assignations, using the values reported in [10]. CF_3-CH_2- 60 ppm; CF_3-CF_2- and CF_3-CFH- 80 ppm; CF_2H-CF_2- and CF_2H-CFH- 130 - 138 ppm; CFH_2-CF_2- and CFH_2-CFH- 230 - 240 ppm). These fluorination patterns are in agreement with the GC/MS results.

Summing up, we found that partially fluorinated compounds are most probably intermediates in electrochemical fluorination reactions of alkylamines, but at the same time polyfluorinated by-products are formed. The inertness of these by-products toward further electrochemical fluorination cannot be explained on the basis of a shielding caused by the fluorine atoms. A more detailed investigation of this phenomenon may afford a deeper insight into ECF-mechanism. As for the structure of the polyfluorinated compounds, they are mostly dibutylmethylamines with about 9 fluorine atoms per molecule on average. The fluorine atoms are almost certainly not bound to α-C-atoms (with respect to N).

EXPERIMENTAL

Electrochemical fluorinations

The ECF of DBMA was carried out batch-wise as well as semicontinuously. Typical conditions of batch-experiments are given in [4]. These experiments were stopped when the current (at constant voltage) dropped significantly, i.e. to about 1/4 of the value at the beginning. In most cases very small explosions occurred at the end of the experiments. In case of the semicontinuous experiments, DBMA was repeatedly added to the cell (and also HF) without interruption of the electrolysis. Intervals and dosage volumes of the DBMA-addition had been arranged such as to restore the original amount of DBMA after applying an electric current which could theoretically perfluorinate 3.7 % of the DBMA. In this way, up to 10 times of the original amount of DBMA (starting concentration 11 %) was added before the electrolysis came to end, due to too high a concentration (about 40 % w/w) of dissolved partially-fluorinated amines in the HF.

Analytical investigations

In both types of experiments samples of the liquid hydrogen fluoride were periodically taken from the cell. The work-up procedure for them is given in [4], it combines treatment with alkali and extraction with ether. The resulting "HF-phases" were analysed as follows: The fluorine content was determined by the WICKBOLDT-method [11]. The molecular weight was determined cryoscopically in benzene. Gas chromatography was carried out using a CHROMATRON GCHF 18.3 machine with packed columns (10 % OV 101 on N-AW-OMCS, 3.7 m x 3 mm, 80 - 100 °C). GC/MS was run on a HP 5985 B GC/MS-system with a 25 m Carbowax column; in EI mode with 70 eV and in CI experiments with isobutane as reactant gas. ^{19}F-NMR spectra were recorded on a 1.4 T (57 MHz) NMR spectrometer FKS 176/178 using TFA as reference compound and acetone as solvent. The values are given relative to $CFCl_3$ ($\delta_{CFCl_3} = \delta_{TFA} +$ 76,5), values upfield to $CFCl_3$ are positive.

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