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THE ELECTROCHEMICAL FLUORINATION OF ORGANIC COMPOUNDS: FURTHER DATA IN SUPPORT OF THE EC_bEC_N MECHANISM

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SUMMARY

Data in support of the four-stage mechanism $\mathrm{EC}_{\mathrm{b}}\mathrm{EC}_{\mathrm{N}}$ result from the electrochemical fluorination of some acyl halides (benzoyl, *n*-butyryl and *iso*-butyryl, benzenesulphonyl and *p*-toluenesulphonyl chlorides) and amines (tripropylamine and N-methylmorpholine).

INTRODUCTION

Since J.H. Simons, about thirty years ago, set up the process for the electrochemical production of perfluorinated organic compounds, several mechanisms have been suggested in order to explain this reaction. According to the one proposed by Simons himself [1], this process starts with the anodic oxidation of fluoride anions to F' radicals, which substitute the hydrogen atoms in the organic molecule after homolysis of the C-H bond (radical mechanism).

Other subsequent theories suppose that the substitution of hydrogen atoms by fluorine atoms occurs by means of nickel fluorides (NiF₃ and NiF₄) as fluorinating agents [2,3], or through the adsorption on the anode of complexes of the organic compound with nickel fluorides [4].

More recently, I.N. Rozhkov produced much experimental evidence in support of the four-stage mechanism (previously proposed by J. Burdon and co-workers [5]) named EC_bEC_N [6]. In the first stage (E) the organic molecule adsorbed on the anode undergoes an electrochemical oxidation to the corresponding radical-cation; a second chemical stage (C_b) follows, during which the saturated organic compounds generally eliminate a proton: the radical formed in this manner is then oxidized to the corresponding cation (third stage, E), which reacts with a fluoride anion (fourth stage, C_N). According to this mechanism the oxidation of the fluoride anions to radicals and a non-ionic origin of the C-F bond are excluded.

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However, most of the data reported by I.N. Rozhkov in support of this mechanism were obtained from experiments carried out at platinum anodes in aprotic solvents, therefore under different conditions from the ones used in the Simons method. Hence some doubt must still arise on the general mechanism for the electrochemical fluorination of organic compounds. The data here reported shed some light on this problem.

EXPERIMENTAL

Our experiments were carried out in the usual Simons cells [7]: the electrolytic bath was always a solution of the organic compound in anhydrous HF; nickel anodes and iron cathodes were employed. No solvent was used. The most interesting data, as far as the reaction mechanism is concerned, were obtained with benzoyl chloride, butyryl and *iso*-butyryl chlorides, benzenesulphonyl and *p*-toluenesulphonyl chlorides, tripropylamine and N-methylmorpholin and are reported in Table 1.

TABLE 1

Experimental data drawn from the electrochemical fluorination of the mentioned organic compounds.

| Organic compound | Moles fed | Volts | mA/cm ² | F-compound found (moles) | Molar yield | |
|--|------------|--------------------|--------------------|---|------------------|--|
| C ₆ H ₅ COC1 | 2.1 | 4.7÷5.0 | 9÷10 | 1.01 | 48.1 % | |
| | 1.8 | 4.7÷4.9 | 9÷10 | 0.82 | 45.5 % | |
| ** | 8.2 | 6.1÷7.0 | 9÷10 | 2.86 | 34.9 % | |
| 0 | 5.3 | 6.0÷7.0 | 9÷10 | 1.72 | 32.4 % | |
| $n-C_3H_7COC1$ | 10.1 | 5.0÷5.5 | 9÷10 | 3.40 (normal) | 33.6 % | |
| iso-C ₃ H ₇ COC1 | 10.9 | 5.0÷5.4 | 9÷11 | 0.16 (180) 1.54 (normal) 2.74 (iso) | 1.6 % | |
| C ₆ H ₅ SO ₂ C1 | 3.5 3.2 | 5.2÷5.7 5.2÷5.6 | 11÷12 10÷11 | 0.68 | 19.4 % | |
| CH ₃ C ₆ H ₄ SO ₂ C1 | 4.5 4.7 | 5.2÷5.7 5.2÷5.8 | 9÷10 9÷10 | 1.23 | 27.3 % 24.9 % | |

RESULTS

a) <u>Benzoyl chloride</u> Several experiments were carried out with this compound in order to maximize the $C_6F_{11}COF$ yield [7]. Among the experimental data obtained, the ones concerning the experiments carried out at rather low potential differences (4.7-5 volts) are particularly interesting. Under these conditions the yields obtained (45-48 %) were always higher than those (32-

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35 %) observed in analogous experiments carried out at higher potential differences (6-7 volts).

Some experiments were also carried out at 4.9-5.1 volts without adding the organic compound to the electrolytic bath, but using a solution of KF in anhydrous HF having about the same concentration and the same conductivity as the organic compound. Under these conditions a very low current density $(1-3 \text{ mA/cm}^2)$ was observed, compared with the one usually observed with the organic compound (15-20 mA/cm²); this means that no electrochemical process occurs at these voltages in the absence of the organic compound.

b) <u>Butyryl and iso-butyryl chlorides</u> In the experiments carried out with these compounds different percentages were observed for the *normal* and *iso* forms, which in both cases were found in the reaction mixture [8]. In particular, from the *normal* butyryl chloride a mixture of the two isomers of the corresponding acyl fluoride was obtained with a molar ratio *normal/iso* form of 21.2 (corresponding to an isomerization of 4.5 %); whereas in the reaction mixture obtained in a similar manner from the *iso*-butyryl chloride a molar ratio *iso/normal* form of 1.8 was found. Therefore in this latter case a higher isomerization (36 %) occurs.

c) Benzenesulphonyl and p-toluenesulphonyl chlorides In the electrochemical fluorination of these compounds, carried out under the same conditions, unexpectedly high yields (25-27 % molar) were found for $CF_3C_6F_{10}SO_2F$ compared to those (18-19 % molar) of $C_6F_{11}SO_2F$ [9]. This behaviour is unexpected since it is well known that the yield of the perfluorinated organic compounds diminishes as the number of the carbon atoms in the molecule increases.

d) <u>N-methylmorpholine and tripropylamine</u> The electrochemical fluorination of tertiary amines [10] has previously been studied also at a rather high concentration (30-40 % wt) of N-methylmorpholine [11] and tripropylamine [12] in anhydrous HF. The experiments were carried out in order to identify the partially fluorinated compounds formed during the electrolytic process, and very interesting data, as far as the reaction mechanism is concerned, were obtained. These data are reported in Table 2 and Table 3.

Moreover, increased molar yields were observed in the series tripropylaminc (10 %) < tributylamine (18.5 %) < tripentylamine (25.4 %) < N-ethylpiperidine (41 %).

DISCUSSION

The experimental data reported give important insights on the mechanism of the electrochemical fluorination of organic compounds in anhydrous HF,

The data for benzoyl chloride show that this process proceeds with satisfactory yields even at voltages too low to allow a substantial discharge of fluorine. This means that the electrochemical fluorination may occur without anodic formation of fluorine radicals. TABLE 2

Percentages of identified compounds in the reaction mixture after a quantity of current, equivalent to 1.5 atoms (column I) and 2.4 atoms (column II) of fluorine per mole of N-methylmorpholine, had passed

| Compound | Column I | Column II |
|--|----------|-----------|
| N-methylmorpholine | 61.3 | 38.3 |
| 2-fluoro-N-methylmorpholine | 19.6 | 28.2 |
| 2,2-difluoro-N-methylmorpholine | 0.9 | 1.9 |
| 2,5-difluoro-N-methylmorpholine | 0.2 | 0.6 |
| 2,6-difluoro-N-methylmorpholine | 4.4 | 9.1 |
| 2,2,6-trifluoro-N-methylmorpholine | 1.6 | 4.4 |
| 2,2,6,6-tetrafluoro-N-methylmorpholine | 0.5 | 1.5 |
| perfluoro-N-methylmorpholine | 6.5 | 11.0 |

TABLE 3

Percentages of fluorinated groups found by NMR analysis of the reaction mixture after a quantity of current, equivalent to 1.5 atoms (column I) and 2.5 atoms (column II) of fluorine per mole of tripropylamine, had passed

| Group | Column I | Column II | |
|--|----------|-----------|--|
| CH ₂ F-CH ₂ -CH ₂ - | 4 4 | 26 | |
| CHF ₂ - CH ₂ - CH ₂ - | 17 | 15 | |
| CH ₃ - CHF - CH ₂ - | 39 | 21 | |
| CH ₂ F-CHF-CH ₂ - | - | 7 | |
| CHF ₂ -CHF-CH ₂ - | - | 4 | |
| CH ₂ F-CHF-CH ₂ - | - |) – | |
| $CHF_2 - CHF - CH_2 -$ | - | } / | |

Moreover, the behaviour observed in the electrochemical fluorination of iso- and n-butyryl chlorides fits an $\mathrm{EC}_{\mathrm{b}}\mathrm{EC}_{\mathrm{N}}$ mechanism. The perfluoro-n-butyryl fluoride found in the reaction mixture obtained from the iso-butyryl chloride could rise from a rearrangement involving a carbocation:

 $\begin{array}{ccc} CH_{3}CHCOF & \xrightarrow{-e} & CH_{3}CHCOF & \xrightarrow{-H^{\bigoplus}} & CH_{3}CHCOF & \xrightarrow{-e} & CH_{3}CHCOF \\ | & & | & | & | & | & | \\ CH_{3} & & \downarrow & CH_{3} & & \vdots \\ \end{array} \xrightarrow{(C_{b})} & \begin{array}{c} CH_{3}CHCOF & \xrightarrow{-e} & CH_{3}CHCOF & \xrightarrow{-e} & \\ \hline & & | & | & | & | & | \\ CH_{2} & & & CH_{2} & & \\ \end{array}$



Due to the relative stability of the carbocations I and II, in the electrochemical fluorination of the *iso* compound a considerable isomerization (36 %) to the *normal* form occurs, whereas in the case of the *normal* compound the reverse isomerization is much lower (4.5 %). The radical mechanism could not explain these isomerizations occurring in the electrochemical fluorinations in anhydrous HF at nickel anodes.

The $\mathrm{EC}_{\mathrm{b}}\mathrm{EC}_{\mathrm{N}}$ mechanism also explains the different yields observed in the electrochemical fluorination of benzenesulphonyl and p-toluenesulphonyl chlorides. In the case of this latter compound the first stages E and C_b can occur more easily than in the case of benzenesulphonyl chloride, because of a greater stabilization of the corresponding radical-cation and radical, due to a larger delocalization:



Thus, the reaction requires less energy and leads more directly to the fluorinated compound. The higher yields observed in the case of p-toluenesulphonyl chloride can also be explained in this manner.

More interesting data were obtained from the experiments carried out with tertiary amines. In the electrochemical fluorination of N-methylmorpholine (Table 2) only one partially fluorinated compound bearing a fluorine atom adjacent to the nitrogen atom was found. The other identified compounds all show the fluorine atoms close to the oxygen atom. This means that the substitution of hydrogen atoms by fluorine atoms does not occur randomly (as it should do if a radical mechanism was operating), but proceeds with some selectivity, starting from the carbon atoms nearest to the oxygen, where the electron density is greater Thus, the substitution of the first hydrogen atom could occur as follows, according to the EC_bEC_N mechanism:



Moreover, N-methylmorpholine was always found in the reaction mixture together with perfluoro-N-methylmorpholine and products of partial fluorination; therefore, the substitution of hydrogen atoms proceeds preferentially in the molecule where it has already commenced. This is in agreement with the $\mathrm{EC}_{\mathrm{b}}\mathrm{EC}_{\mathrm{N}}$ mechanism, according to which the fluorination occurs at the molecules adsorbed on the anode. In these molecules the reaction proceeds until there is complete substitution of hydrogen atoms; after this, the perfluorinated molecule breaks off the electrode and moves into the bath.

The experiments carried out with tripropylamine confirm this interpretation of the electrochemical process of fluorination. The data reported in Table 3 indeed show a preferential substitutio of the farthest hydrogen atoms from the positive charge localized on the nitrogen atom. The substitution of hydrogen atoms starts on these far carbon atoms immediately after the oxidation of the adsorbed molecule. Similarly it is possible to explain the sequence of yields observed in the series tripropylamine, tributylamine, tripentylamine and N-ethylpiperidine: in the case of a radical mechanism an inverse pattern of yields should have been found.

CONCLUSIONS

The data here reported support the EC_bEC_N mechanism. Although some of them could be the result of a radical mechanism (<u>i.e</u>, the electrochemical fluorination of benzenesulphonyl and *p*-toluenesulphonyl chlorides), the other data and especially those obtained from the experiments carried out with N-methylmorpholine and tripropylamine are clearly in favour of the EC_bEC_N mechanism.

On the other hand, the radical fluorination cannot be completely excluded in the electrolytic process and must be considered as a secondary side reaction, that becomes more and more important as the voltage at the electrodes increases.

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