Journal of Fluorine Chemistry, 60 (1993) 57–60

On the electrochemical fluorination of quaternary ammonium compounds. Part 1. Tetraalkyl ammonium salts*

A. Dimitrov, W. Radeck, St. Rüdiger
Project Group Fluorine Chemistry, sponsored by KAI e.V., Geb. 4.1, Rudower Chaussee 5, 0-1199 Berlin (Germany)

O. Bechstein
Fachbereich Chemie, Institute of Inorganic Chemistry, Humboldt-University, Hessische Str. 1-2, 0-1020 Berlin (Germany)

(Received December 12, 1991; accepted March 4, 1992)

Abstract

Tetraalkylated ammonium compounds, which are known to be very stable towards oxidative attack, can be electrofluorinated readily to yield perfluoro tertiary amines. Other than the enhanced formation of gaseous cleavage products, the electrofluorination proceeds similarly to that of other tertiary amines.

Introduction

Tetraalkylammonium cations are very stable towards oxidative attack. As a result, their salts are used as stable, conductive and soluble additives in organic electrochemistry, e.g. in the electrofluorination in organic solvents [1]. The high stability of the tetramethylammonium cation towards oxidative fluorination makes it a valuable cation in the stabilization of higher valent halogen fluoride anions [2]. However, trialkylammonium cations, which are formed if trialkylamines are dissolved in HF, can be electrochemically fluorinated readily in HF, despite also having a high oxidation potential [3]. This makes a mechanism involving a primary electrochemical oxidation step somewhat unlikely. Hence, it is of interest to study the electrofluorination of tetraalkylated ammonium compounds.

Results and discussion

The quaternary ammonium compounds which were subjected to electrochemical fluorination (ECF) and the results of these reactions are listed in Table 1. From this table it can be seen that all the compounds studied generate perfluorinated tertiary amines, with some in quite good yield. It is

---

*Presented, in part, at the 13th Int. Symp. Fluorine Chem., Bochum, Germany, 1991.

0022-1139/93/$6.00

TABLE 1

Electrofluorinated quaternary ammonium compounds and their perfluoro products

Starting compound	Yield (%)[a]	Liquid perfluorination products (%)
$(C_4H_9)_3\ (C_2H_5)N^+\ I^-$ (**1**)	19.6[b]	$(C_4F_9)_2NC_2F_5$ (**6**) (78.5%) $(C_4F_9)_3N$ (**7**) (21.5%)
$(C_4H_9)_2\ (C_2H_5)\ (CH_3)N^+\ I^-$ (**2**)	10.2[c]	$(C_4F_9)_2NC_2F_5$ (**6**) (57%) $(C_4F_9)_2NCF_3$ (**8**) (25%) $(C_4F_9)\ (C_2F_5)_2N$ (**9**) (11%) $(C_4F_9)\ (C_2F_5)NCF_3$ (**10**) (6.6%)
$(C_4H_9)_4N^+\ Br^-$ (**3**)	38[d]	$(C_4F_9)_3N$ (**7**) (63.7%)
$(C_4H_9)_4N^+\ BF_4^-$ (**4**)	22[d]	$(C_4F_9)_3N$ (**7**) (78%)
$(C_2H_5)_4N^+\ I^-$ (**5**)	38.3[d]	$(C_2F_5)_3N$ (**11**) (70%)

[a] Total yield of liquid perfluorination products calculated on the following bases: [b] for the actual mixture; [c] for $(C_4F_9)_2NC_2F_5$; [d] for the actual F-amine.

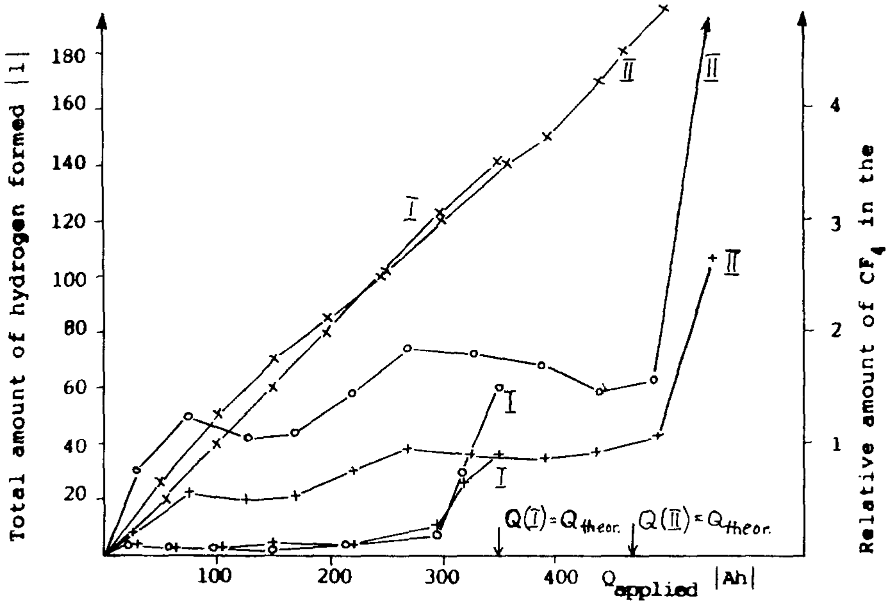

Fig. 1. Formation of H_2 (×), CF_4 (○) and NF_3 (+) during the ECF of $(C_4H_9)_3N$ (curves I) and $(C_4H_9)_4NBF_4$ (curves II).

obvious that their formation is linked with the splitting off of one alkyl group. As a result, significantly more gaseous fluorination products are formed than with tertiary amines. A direct comparison of the ECF of tributylamine with that of compound **4** shows that the latter yields more than 10 times the amount of gaseous fluorination products than tributylamine (Fig. 1). However, the relative amount of NF_3 formed also increases, indicating that the gaseous products not only stem from the eliminated alkyl group but also from the enhanced total cleavage.

Compounds with more than one type of alkyl group yield the respective perfluoro tertiary amines. The results listed in Table 1 do not allow a decision as to whether the splitting off of a particular alkyl group is dependent on its nature (in compound **2**, the methyl group is obviously more likely to leave the molecule than the others) or only on its relative abundance (as indicated by the products of compound **1**). Another question which we are about to study is at what degree of fluorination or what point of the fluorination pathway the leaving alkyl group actually splits off. To provide an answer it is obviously necessary to investigate the partially fluorinated compounds when dissolved in the HF. Here we report only the results concerning the perfluoro products.

In total, the results show that quaternary ammonium compounds can be electrochemically fluorinated readily, despite their well-known stability towards oxidative attack. We consider these results as further evidence for an ECF mechanism which does not necessarily involve primary electrochemical oxidation of the substrate.

Experimental

The electrochemical fluorinations were carried out in a 450 ml stainless-steel or all-PTFE cell, as described elsewhere [4]. Fluorination products were refluxed with conc. aqueous KOH, distilled off and identified by GC methods using an authentic sample, or by GC–MS.

Gas chromatography was undertaken on a CHROMATRON GCHF 18.3 instrument with packed columns (10% FS 16 on N-AW-DMCS, 3.7 mm, 3 m; for gaseous perfluorination products, the column was packed with Porapak Q). GC–MS was carried out using a Finnigan MAT GC–MS system 5100 (quadrupole). For GC, a 50 m column packed with SE 30 was employed; MS studies were undertaken in the EI mode at 90 eV.

Syntheses of starting compounds

Compound **1** was obtained by reacting commercial tributylamine with C_2H_5I, whereas compound **2** was prepared by methylating commercial dibutylamine with HCHO/HCOOH (Leuckart–Wallach reaction) and subsequent reaction with C_2H_5I. Compounds **3** and **5** were both commercial products. Finally, compound **4** was obtained by reacting commercial tetrabutylammonium iodide with HBF_4. The crude **4** obtained was recrystallized three times from EtOAc/pentane.

Perfluorinated products

In addition to the liquid fluorination products listed in Table 1, and discussed in the following, every run also produced gaseous products, mainly

CF_4 and NF_3 (see Fig. 1), whose presence was confirmed by GC methods using authentic samples.

Compound **6**: MS *m/z*: 502 $[M-CF_3]^+$; 402 $[M-C_3F_7]^+$; 314 $[C_6F_{12}N]^+$; 219; 131; 119; 100; 69 (basis peak).

Compound **7**, compound **8** and compound **11**: confirmed by GC methods in comparison with authentic samples.

Compound **9**: MS *m/z*: 402 $[M-CF_3]^+$; 314 $[C_6F_{12}N]^+$; 302 $[M-C_3F_7]^+$; 264; 164; 131; 119; 69 (basis peak).

Compound **10**: MS *m/z*: 352 $[M-CF_3]^+$; 252 $[M-C_3F_7]^+$; 219; 164; 131; 119; 114; 69 (basis peak).

References

1 I. N. Rozhkov and I. Y. Alyev, *Tetrahedron, 31* (1975) 977.
2 K. O. Christe and W. W. Wilson, *J. Fluorine Chem.*, *45* (1989) 4.
3 A. Dimitrov, St. Rüdiger, N. V. Ignatyev and S. Datcenko, *J. Fluorine Chem.*, *50* (1990) 197.
4 A. Dimitrov, H. Stewig, St. Rüdiger and L. Kolditz, *J. Fluorine Chem.*, *47* (1990) 13.