Journal of Fluorine Chemistry, 30 (1985) 89–95

Received: February 12, 1985; accepted: June 13, 1985

CORRELATION BETWEEN YIELD AND OPERATING CONDITIONS IN THE ELECTROCHEMICAL FLUORINATION OF TRIPROPYLAMINE

L. CONTE, M. NAPOLI and G.P. GAMBARETTO

Institute of Industrial Chemistry, University of Padua, via
Marzolo 9, 35131 Padua (Italy)

SUMMARY

Electrochemical fluorination of tripropylamine in anhydrous hydrogen fluoride was studied in order to verify the correlation between the operating conditions and the yield of the corresponding perfluoroamine. The parameters tested were: temperature, voltage, initial concentration of amine in the bath, constant concentration of amine in the bath and stirring effect. Experimental data show that temperature is the parameter exerting the most remarkable influence over perfluoroamine yield and by-products formation.

INTRODUCTION

Recent employments of great interest have been found for some perfluorinated tertiary amines in the medical (oxygen carrier liquids, artificial blood) and electronic (high voltage insulators, heat transfer in soldering) fields. For this reason a particular attention has been paid to the electrochemical fluorination of amines in anhydrous hydrogen fluoride, which is at present the only important process, from the commercial aspect, for preparing these compounds.

Unfortunately, this electrochemical process generally exhibits low yields of perfluorinated tertiary amines: values of about 27% were reported for triethylamine [1]; in previous experiments we have found molar yields of about 25% for tripentylamine and 18% for tributylamine[2]. Such a low yields are principally due to side reactions of degradation and rearrangement that are usual in the electrochemical fluorination, and to an incomplete substitution of hydrogen atoms by fluorine in the organic molecule. Therefore, the reaction mixture is always rather complex and the numerous by-products make the perfluoroamine isolation very difficult.

0022-1139/85/3.30

An improvement of the yield for this process is evidently desirable; for this reason some research have been done by us on the influence of the operating conditions used in the electrochemical fluorination. The results of our experiments with tripropylamine (TPA) are reported here.

EXPERIMENTAL

A Simons-type cell described elsewere [3] was used, with nickel electrodes and an effective anodic area of 772 cm^2. The total volume of the electrolytic bath was 1.1 liter. Hydrogen fluoride was electrochemically dehydrated before each experiment. Tripropylamine was always converted into the corresponding HF adduct by treatment with hydrogen fluoride before being fed into the cell.

The amount of current required for the complete fluorination of the amine fed was calculated as follows:

$$Q = 59.4 \cdot M \cdot H \quad \text{Amph} \qquad (1)$$

where:

M = moles of amine fed;

H = hydrogen atoms per mole of amine;

59.4 = Amph required for the development of one mole of fluorine with a current yield of 90%.

The experiments were carried out varying the following parameters:

- initial concentration of TPA in the electrolytic bath;
- voltage;
- temperature of the electrolytic bath (this was kept constant by means of a cooling fluid coming from a cryostat and circulating into the interspace of the cell).

Some experiments were carried out keeping constant the TPA concentration in the bath, by periodically adding amounts of amine equivalent to the amount of current passed; and stirring the bath by nitrogen bubbling into the interelectrode space.

For each experiment the reaction products were periodically extracted from the bottom of the cell, where they tended to deposit being insoluble and heavier than HF. The amounts recovered in this manner were collected and subjected to GLC analysis after treatment with aqueous $NaHCO_3$. In some experiments also the products soluble in the bath were recovered by removal of HF by a stream of nitrogen however, negligible amounts of organic compounds were obtained in this manner; their values are not included in the figures presented in the Table.

Analytical GC work was performed by a Perkin-Elmer Sigma 3 gas-chromatograph using a stainless steel column (5 mm i.d., 2 m long) packed with 20% Fomblin Y25 on Chromosorb P silanized (100-120 mesh). Temperatures: 120 °C for column, 150 °C for injector and detector. Carrier gas: hydrogen at 33 ml/min. The normalized areas method was used for quantitative data.

RESULTS AND DISCUSSION

Experimental data are reported in the Table, together with the operating conditions used for the experiments. F-TPA data and yields are relative to unisomerized perfluorinated compound.

TABLE

Experimental data and operating conditions for the electrochemical fluorination of TPA

	TPA fed			volts	°C	reaction	F-TPA		molar
	g	moles	% wt	(mean value)		mixt.(g)	% wt	moles	yield (%)
1	115	0.80	10	5.6	19	47	68.9	0.06	7.5
2	245	1.71	20	5.6	19	175	70.7	0.24	14.0
3	267	1.87	25	5.6	19	189	71.1	0.26	13.9
4	228	1.59	10	5.3	19	139	69.5	0.18	11.3
5	85	0.59	10	5.6	-4	110	72.2	0.15	25.4
*6	251	1.75	10	5.6	-4	339	71.8	0.47	26.8
**7	128	0.89	10	5.6	-4	180	72.3	0.25	28.1

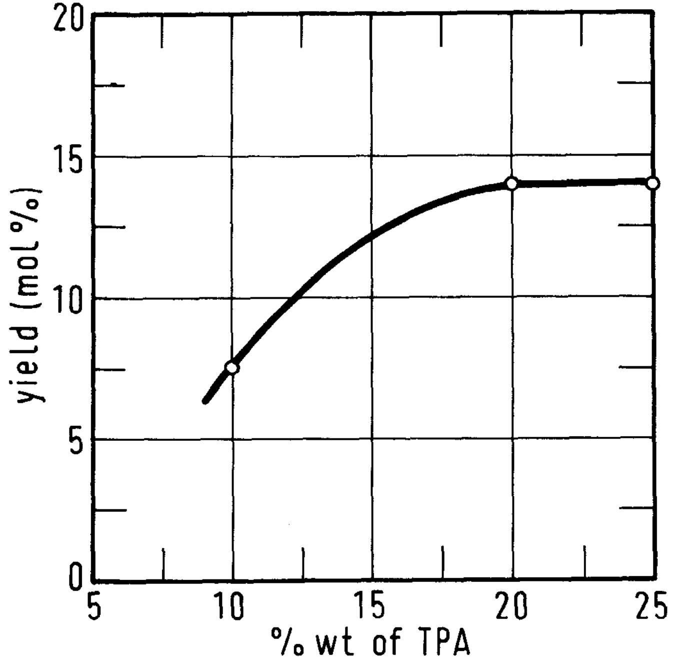
*TPA concentration kept constant
**bath stirred

The following remarks summarize the influence of the operating conditions on F-TPA yield.

a) Initial concentration of TPA.- Data from experiments 1, 2 and 3 show how the F-TPA yield changes with the initial concentration of TPA in the electrolytic bath. In particular, an improvement of the yield results as the initial concentration of amine increases. However, as shown in Fig. 1 (where yield is plotted against % wt), this improvement is modest and ends at concentrations higher than 20% wt.

b) Voltage The effects of change of the cell voltage are shown in experiments 2 and 4: even a small voltage drop results in a lowered F-TPA yield.

c) Temperature An increase in yield results from a lowering of bath temperature. Data from experiments 1 and 5 show a three-fold increase of F-TPA yield when temperature changes from 19 to -4 °C. But temperature also acts on the bath conductivity as shown in Fig. 2: so, experiments carried out at low temperature took longer. However, this greater time is more than balanced by higher yields. So, in experiment 1, 31.3 g of F-TPA were obtained in about 62.5 hours (with a mean production of 0.5 g/h), while in experiment 5, 78.1 g of F-TPA were obtained in about 51.2 hours



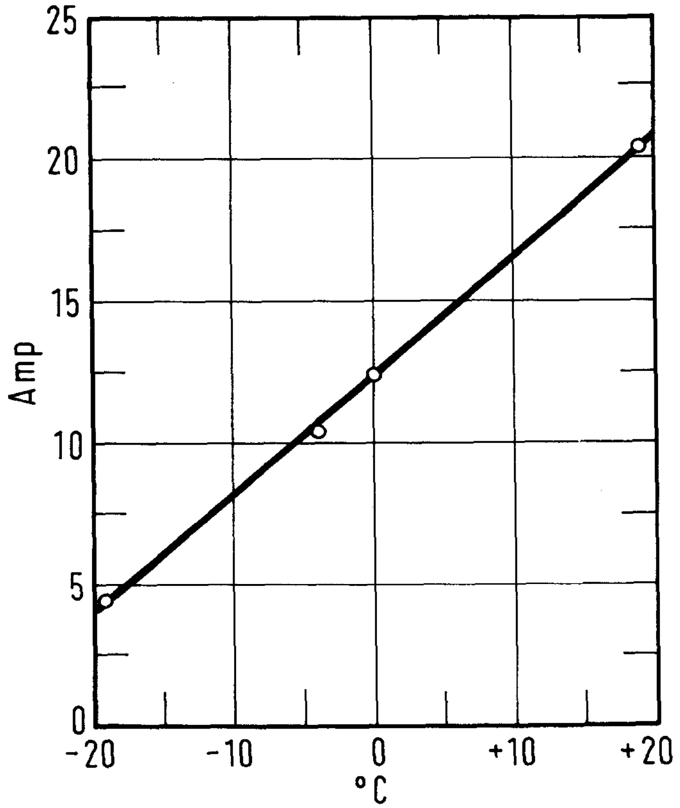


Fig. 1. F-TPA yield (mol%) plotted against the initial concentration of TPA in the electrolytic bath.

Fig. 2. Plot of current intensity versus temperature in the electrolytic bath containing 10% wt of TPA in anhydrous HF.

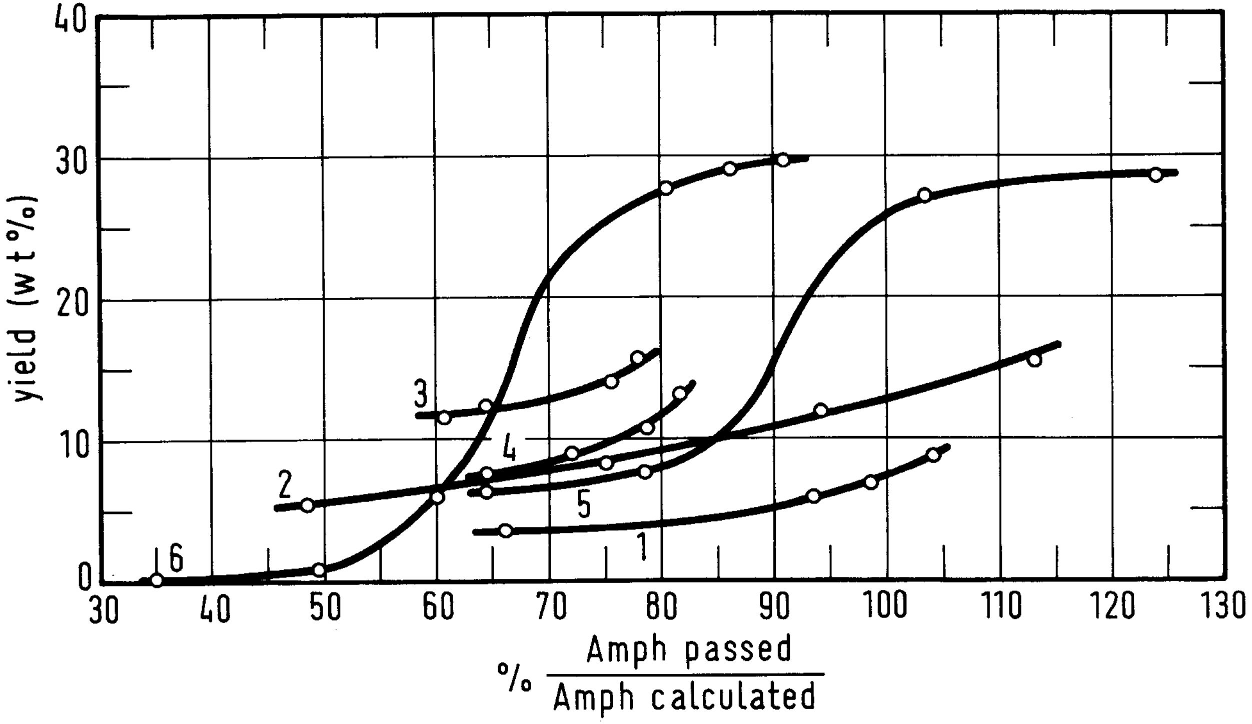


Fig. 3. Plot of the reaction mixture yield (% wt based on theoretical amount of the corresponding amine fed) versus the ratio between Amph passed and Amph calculated for each experiment.

(with a mean production of 1.5 g/h). Therefore, at -4 °C the F-TPA production per unit of time was three times higher than that obtained at 19 °C.

d) Constant concentration of TPA In experiment 6 successive amounts of TPA, equivalent to the current amounts passed, were fed into the electrolytic bath as the reaction products were extracted from the cell, so that the TPA concentration in the bath could be considered unchanged for about 90% of the process time. A small increase in F-TPA yield can be observed comparing experiments 6 and 5. The F-TPA production per unit of time increase to 2.5 g/h. However, these modest improvements do not balance the great complications resulting from carrying out the process in this manner.

e) Stirring effect A small increase in F-TPA yield results from bath stirring (compare data from experiments 7 and 5). Also the amount of F-TPA produced per unit of time is quite high (2.3 g/h), but considerable amounts of HF were removed by the nitrogen stream, so that periodical additions of HF were needed in order to restore the bath level.

Fig. 3 shows the yield change during each experiment. Yield is here plotted against the ratio between the Amph passed and those calculated from equation (1). Since F-TPA % wt in the reaction mixture was almost the same for all experiments (see the Table), the yield is here expressed as a ratio between the amount of the reaction mixture recovered and that calculated from the amount of TPA fed.

CONCLUSIONS

Experimental data show that the yield of the electrochemical fluorination of TPA is influenced by the operating conditions. The most marked changes are caused by the initial concentration of the amine and especially by the temperature.

The favourable effect due of a lowering of temperature is certainly related to a consequent lowering of degradation and decomposition reactions [4]: at the end of experiments carried out at low temperature the electrolytic bath was cleaner, less coloured and more transparent than those formed at higher temperature.

ACKNOWLEDGEMENTS

This work has been carried out with the financial support of C.N.R. (Consiglio Nazionale delle Ricerche), Roma.

REFERENCES

1 T. Abe and S. Nagase, in R.E. Banks (ed.), 'Preparation, Properties and Industrial Applications of Organofluorine Compounds', 1982, p. 35.

2 Unpublished results.

3 C. Fraccaro, M. Napoli and L. Conte, Atti Ist. Ven. SS.LL.AA., CXXXIX (1980-1981) 203.

4 B. Chang, H. Yanase and N. Watanabe, Electrochem. Acta, 16 (1071) 1179.